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THE BEHAVIOUR  
OF SLOW ELECTRONS  
IN GASES



# THE BEHAVIOUR OF SLOW ELECTRONS IN GASES

AN ACCOUNT OF DIFFUSION METHODS TOGETHER WITH A  
COMPARISON BETWEEN RESULTS OBTAINED BY THESE AND  
BY VARIOUS OTHER METHODS

BY

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TO  
VIOLET  
WHO LIGHTENED THE  
TASK OF WRITING  
THIS BOOK



## PREFACE

This book is intended to give a brief, critical survey of the work on the behaviour of slow electrons in gases, much of which has been carried out during the last twenty-five years and is available only in the original communications. The investigations described deal with the determination of such quantities as the mean free paths, average energy losses and probabilities of attachment, of electrons moving through a gas with energies not exceeding a few electron volts.

Many different techniques have been used for the investigation of the various aspects of the motion of electrons in gases. Here the main attention is focussed on the diffusion methods developed by Townsend at Oxford and by Bailey at Sydney, as these lead to the widest variety of experimental results; particular attention is given to the study of the formation of negative ions by attachment.

An account of the diffusion methods is given in the earlier chapters, including a discussion of the formulae used and a summary of the experimental results obtained. There follows a brief survey of a number of other methods. An important application of the work described in the earlier portion of the book is given in the final chapter which is devoted to certain problems concerning the motion of electrons in alternating fields and the effect of radio waves on the ionosphere.

The book should be useful as a work of reference, for essentially all of the results obtained by the diffusion methods are given by means of graphs and tables, and the bibliography relating to the whole field is comprehensive. The final chapter should be of interest to those concerned with the propagation of radio waves. Further, we have endeavoured to make the presentation sufficiently complete and straightforward to prove of value to the general physicist, and to Physics students in the final years of a degree course.

The authors wish to acknowledge their indebtedness to Professor V. A. Bailey for the benefit of a number of helpful discussions, and to Mr. N. F. Roberts for his assistance in the preparation of the manuscript for publication; finally they wish to thank Miss D. Grime for her help in proof reading and Messrs. Simmons Limited for their patience and care in the printing of the book.

R.H.H.  
J.W.R.

SYDNEY  
*November, 1940.*





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THE BEHAVIOUR  
OF SLOW ELECTRONS  
IN GASES



# I

## THE MOTION OF SLOW ELECTRONS IN GASES

### 1.1—Maxwell's Diffusion Equations.

Maxwell's theory of diffusion was first developed to account for the interdiffusion of two gases. Later, J. S. Townsend made a natural application of this theory to the case in which one gas is replaced by a swarm of electrons or ions\*. Most of the methods described in this book for investigating the motion of electrons in a gas depend upon the kinetic diffusion of these particles as they pass through the gas; accordingly, the fundamental equations relating to the process of diffusion are introduced immediately.

We begin by introducing an important quantity, the coefficient of diffusion  $K$ , which is defined† as "... the volume of gas reduced to unit of pressure which passes in unit time through unit of area when the total pressure is uniform . . . . and the pressure of either gas increases or decreases by unity in unit distance." In all the diffusion experiments described in the present book the partial pressure of the charged particles has been small compared with that of the gas, so that the total pressure may be regarded as uniform. Under these conditions the equation of diffusion takes a simplified form, the net transport of the charged particles per second across unit surface normal to the pressure gradient being

$$P\mathbf{V} = -K \cdot \text{grad } P, \quad \dots\dots\dots(1)$$

in which equation  $P$  is the partial pressure and  $\mathbf{V}$  the transport velocity of the particles. In the Cartesian form, this equation becomes

$$\frac{PV_x}{K} = -\frac{\partial P}{\partial x}, \text{ etc., } \dots\dots\dots(2)$$

$V_x$ ,  $V_y$  and  $V_z$  being the components of  $\mathbf{V}$ . The term  $-(\partial P/\partial x)$

\* J. S. Townsend, *Phil. Trans.*, A, 193, p. 129 (1899).

† J. C. Maxwell, "Collected Papers," 2, p. 60.

represents the momentum parallel to the  $x$ -axis transferred to unit volume per second by the flow of the charged particles across its bounding surface.

Under the conditions usually encountered, it may reasonably be presumed that the mean velocity of agitation  $\bar{U}$  and the velocity-distribution of the particles do not vary from point to point; so that the root mean square velocity  $u$  and hence the mean energy of agitation  $E$  are taken to be the same at all points in the gas. Then, from the equation

$$P = \frac{1}{3} nm u^2, \quad \dots\dots\dots(3)$$

in which  $n$  is the particle density at the point considered and  $m$  is the mass of the particle, it will be seen that the equations (2) may be written

$$nV_x = -K \frac{\partial n}{\partial x}, \text{ etc. } \dots\dots\dots(4)$$

With this notation, the equation of continuity,

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial x}(nV_x) + \frac{\partial}{\partial y}(nV_y) + \frac{\partial}{\partial z}(nV_z) = 0, \quad \dots\dots(5)$$

becomes

$$\frac{\partial n}{\partial t} - K \left( \frac{\partial^2 n}{\partial x^2} + \frac{\partial^2 n}{\partial y^2} + \frac{\partial^2 n}{\partial z^2} \right) = 0. \quad \dots\dots(6)$$

It is necessary to point out that the transport velocity, which in general varies from point to point in the gas, should not be confused with the mean agitational velocity  $\bar{U}$ , which is usually presumed to be constant under the given conditions. The velocities  $V_x$ ,  $V_y$  and  $V_z$  are to be regarded as mathematical quantities which satisfy the condition that the change in the distribution which would obtain if all the charged particles in any volume element had the velocities  $V_x$ ,  $V_y$  and  $V_z$  corresponding to this element, and no other motion, should be the same as the actual change in distribution arising from the motion of agitation\*. Further, it must be emphasised that the velocities  $V_x$ ,  $V_y$  and  $V_z$  do not represent a general drift arising from the variation of  $n$  from point to point; these quantities are introduced merely to describe the net

\* Townsend, *Phil. Mag.*, 25, p. 459 (1938).

rate of kinetic diffusion from an element of space into neighbouring elements. In this respect the velocity  $\mathbf{V}$  differs from the mean drift velocity  $\mathbf{W}$  due to an applied uniform electric field,  $\mathbf{W}$  representing a general drift of all the charged particles in a direction parallel to the field.

## 1.2—Early Experimental Work.

The early experiments\* on the motion of ions in gases were made at relatively high pressures ( $\sim 760$  mm). It was found that the drift velocity of the ions was small compared with that which would be attained under similar circumstances by a gas molecule carrying unit charge; and also that the coefficients of diffusion in air at atmospheric pressure were considerably smaller for ions than for gas molecules. These results led to the conclusion that, at higher pressures, the masses associated with the atomic charges were large compared with the masses of the corresponding gas molecules. However, later experiments showed that, as the gas pressure was reduced, the mass associated with the atomic charge became smaller; in dry gases, at pressures not greater than about 10 mm, and with electric forces of several volts per centimetre, the negative particles attained very high velocities, indicating that the masses of a large proportion of these particles were considerably smaller than the corresponding molecular masses.

Townsend determined the charge carried by a gaseous ion by measuring the lateral diffusion of a stream of ions moving in a uniform electric field. The apparatus used is shown diagrammatically in figure 1. X-rays from a source  $X$  were passed through an aluminium window at the top of the apparatus and fell on the metal plate  $T$ , giving rise to secondary X-rays. These secondary rays ionized the gas, some of the ions passing through the gauze accelerating-electrode  $G$ , and of these, a proportion passed through a circular orifice  $S$ . These ions moved through the uniform electric field produced by the guard-rings  $R_0$ ,  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$ , falling finally on the composite electrode  $AB$ , which consisted of a disc  $B$  and an outer ring  $A$  coaxial with  $S$ . The measurement consisted in determining the ratio  $R$  of the current arriving on  $B$  to that

\* See Townsend, "Electricity in Gases," 1915; "Motion of Electrons in Gases," 1925.

arriving on  $A$ . The value of  $Ne$  was then calculated from this result,  $N$  being the number of molecules in 1 cc of a gas at  $15^\circ\text{C}$  and 760 mm, and  $e$  the charge carried by a gaseous ion.

The formulae used in the calculation referred to above were derived from a theoretical consideration of the diffusion of ions in a uniform electric field.

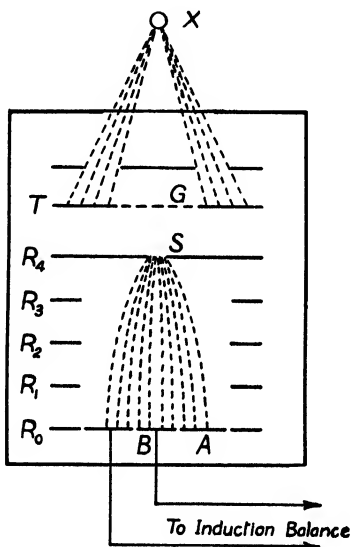


FIG. 1. Schematic diagram of Townsend's diffusion apparatus.

### 1.3—The Diffusion of Charged Particles in a Uniform Electric Field.

When a uniform electric field  $\mathbf{F}$  is applied, there is a general drift of all the charged particles in a direction parallel to the field, this drift being represented by the drift velocity  $\mathbf{W}$ .

Under these circumstances, the drift velocity may be regarded as superposed on the velocity of transport due to diffusion; so that the number of particles crossing an area  $d\mathbf{S}$  per second becomes

$$(-K \text{ grad } n + n\mathbf{W}) \cdot d\mathbf{S}. \quad \dots\dots\dots(7)$$



If, now,  $\mathbf{V}$  (and its components  $V_x$ ,  $V_y$  and  $V_z$ ) denotes the net transport velocity, we have

$$n\mathbf{V} = -K \text{grad } n + n\mathbf{W}; \quad \dots\dots\dots(8)$$

or, writing this equation in the Cartesian form,

$$nV_x = -K \frac{\partial n}{\partial x} + nW_x, \text{ etc.}, \quad \dots\dots\dots(9)$$

$W_x$ ,  $W_y$  and  $W_z$  being the components of  $\mathbf{W}$ .

Using the same argument as in §1.1, it is easily shown that the equations (9) may be written

$$\frac{PV_x}{K} = -\frac{\partial P}{\partial x} + \frac{PW_x}{K}, \text{ etc.} \quad \dots\dots\dots(10)$$

In the absence of  $\mathbf{F}$ , these equations are (see §1.1)

$$\frac{PV_x}{K} = -\frac{\partial P}{\partial x}, \text{ etc.} \quad \dots\dots\dots(2)$$

The term on the right represents the momentum parallel to the  $x$ -axis transferred to unit volume per second by the flow of charged particles across its bounding surface; so that the term on the left gives the component of momentum lost in collisions with gas molecules per unit volume per second under the steady velocity of transport  $V_x$ . It is, of course, assumed that the partial pressure of the particles is small compared with that of the gas, so that we need consider only those collisions between particles and gas molecules.

When the field  $\mathbf{F}$  is applied, the component of momentum communicated to unit volume per second becomes  $-\partial P/\partial x + neX$ , the components of  $\mathbf{F}$  being  $X$ ,  $Y$  and  $Z$ , and  $e$  being the charge carried by a particle; while that lost per second in collisions is again equal to  $PV_x/K$ ,  $V_x$  now representing the net velocity of transport given by equation (10). The equations giving the net velocities of transport may therefore be written

$$\frac{PV_x}{K} = -\frac{\partial P}{\partial x} + neX, \text{ etc.} \quad \dots\dots\dots(11)$$

It is usually found convenient to select the coordinate axes so that the  $z$ -axis is parallel to the electric field. Then, repre-

senting the drift velocity of the particles in the direction of this axis by  $W$ , and the electric force by  $Z$ , equations (10) and (11) become

$$\left. \begin{aligned} \frac{PV_x}{K} &= -\frac{\partial P}{\partial x}, \\ \frac{PV_y}{K} &= -\frac{\partial P}{\partial y}, \\ \frac{PV_z}{K} &= -\frac{\partial P}{\partial z} + \frac{PW}{K}, \end{aligned} \right\} \dots\dots\dots(10a)$$

and

$$\left. \begin{aligned} \frac{PV_x}{K} &= -\frac{\partial P}{\partial x}, \\ \frac{PV_y}{K} &= -\frac{\partial P}{\partial y}, \\ \frac{PV_z}{K} &= -\frac{\partial P}{\partial z} + neZ. \end{aligned} \right\} \dots\dots\dots(11a)$$

A comparison of equations (10a) and (11a) leads to the important relationship

$$\frac{W}{K} = \frac{neZ}{P}. \quad \dots\dots\dots(12)$$

As  $P = \frac{1}{3} nm\bar{u}^2$ , it is easily shown that this equation can be written

$$\frac{W}{K} = \frac{NeZ}{k\Pi}, \quad \dots\dots\dots(13)$$

where  $N$  is the number of gas molecules in 1cc of gas at 760 mm and 15°C,  $\Pi$  is the pressure 760 mm expressed in dynes per square centimetre, and  $k$  is the ratio of the mean energy of agitation of the charged particles to that of the gas molecules at 15°C. This equation was first established by Townsend\*.

The equation of continuity of the particles is

$$\frac{\partial n}{\partial t} + \text{div } n\mathbf{V} = 0. \quad \dots\dots\dots(14)$$

The measured ratio  $R$  (see §1.2) is independent of fluctuations

\* *Phil. Trans.*, A, **193**, p. 129 (1899).

in the intensity of the stream of particles, so that the current density at any point may be regarded as constant\*. In this case  $\partial n / \partial t$  is zero. Then, from equation (10a), remembering that  $P$  is proportional to  $n$  under the given conditions, it follows that the particle density  $n$  satisfies the equation

$$\nabla^2 n = \frac{W}{K} \cdot \frac{\partial n}{\partial z}; \quad \dots\dots\dots(15)$$

or, alternatively,

$$\nabla^2 n = \frac{NeZ}{k\Pi} \cdot \frac{\partial n}{\partial z}. \quad \dots\dots\dots(15a)$$

In obtaining equations (15) and (15a), it is assumed that, under the experimental conditions, the ratio  $W/K$  does not vary from point to point. In practice this condition is ensured by causing the stream of particles to traverse several centimetres of the gas before entering the main body of the apparatus (see figure 1), so that a steady state is attained, a steady state being defined as the state in which the average energy lost by a particle at a collision with a molecule is equal to the average work done on the particle by the field between successive collisions. Further, it has been assumed that the density of the particles at any point is so small that effects due to the mutual repulsion of the particles may be neglected. As the currents used in the diffusion experiments are of the order of  $10^{-12}$  amp, this neglect is justified†.

The solution of equation (15a) can be given in the form

$$n = \Phi \left( \frac{NeZ}{k\Pi}, x, y, z \right);$$

and integrating over the electrodes  $A$  and  $B$ , the ratio  $R$  is obtained :

$$R = \Psi \left( \frac{NeZ}{k\Pi} \right).$$

The solution  $\Psi$  for a given apparatus is most conveniently represented by means of a curve, this curve being known as "the normal distribution curve." Such curves have been calculated by Hasel-

\* See Townsend, "Electricity in Gases," pp. 94 and 163.

† See Townsend, *loc. cit.*, p. 128.

foot, Townsend and Tizard, Mackie, Townsend and Bailey\*. A typical distribution curve for an apparatus similar to that shown in figure 1 is given in figure 2.

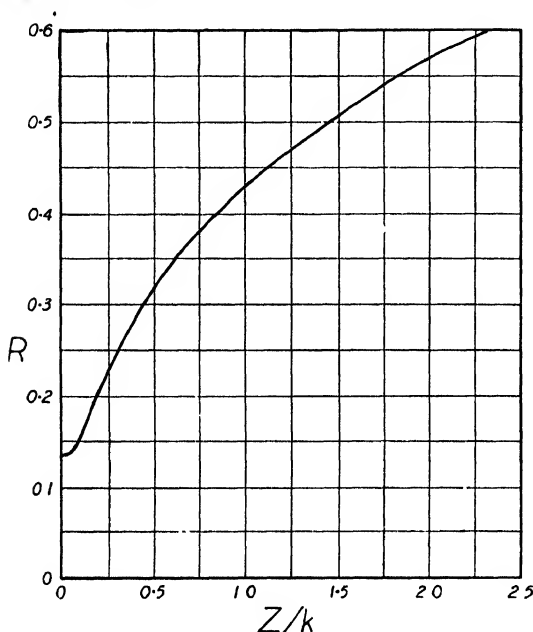


FIG. 2. A typical normal distribution curve.

As most of the early experiments, including that described in §1.2, were carried out under conditions such that only ions were present in the gas, the value of the energy factor  $k$  was unity, as in the steady state the energy of agitation of the ions is very nearly equal to that of the molecules†. Accordingly, knowing the normal distribution curve for the particular apparatus and the value of  $Z$ , an estimate of the quantity  $Ne$  could be made from a single observation of  $R$ .

For negative ions produced by secondary X-rays, the values obtained for  $Ne$  were in excellent agreement with the value  $1.22 \times$

\* Haselfoot, *Proc. Roy. Soc., A*, **87**, p. 350 (1912); Townsend and Tizard, *Proc. Roy. Soc., A*, **88**, p. 336 (1913); Mackie, *Proc. Roy. Soc., A*, **90**, p. 69 (1914), Townsend and Bailey, *Phil. Mag.*, **44**, p. 1013 (1922)

† See "Motion of Electrons in Gases," p. 10.

$10^{10}$  e.s.u. obtained for univalent ions from experiments on electrolysis. The mean values of  $Ne$  determined by Townsend\* were  $1.23 \times 10^{10}$  in air, oxygen and hydrogen, and  $1.24 \times 10^{10}$  in carbon dioxide. Very similar results were obtained when the ions were produced either by a radioactive substance or by photo-electrons liberated from a metal cathode by the action of ultra-violet light†.

The values of  $Ne$  obtained for positive ions were frequently somewhat larger, indicating that a proportion of the ions carried a double charge‡.

The results given above, which support the less accurate values obtained previously§ by substituting experimental values of  $W$  and  $K$  in the equation

$$\frac{W}{K} = \frac{NeZ}{k\bar{M}},$$

show that gaseous ions usually carry a charge equal to that carried by a univalent ion in electrolysis. The close agreement between the results obtained by the methods of electrolysis and diffusion is good evidence that the differential equation for  $n$ , upon which the diffusion method rests, is correct when the charged particles are of molecular mass.

#### 1.4—The Mean Energy of Agitation of Electrons.

In experiments on the lateral diffusion of negative ions, it was found that, for dry gases, when the ratio of the electric force  $Z$  to the gas pressure  $p$  was not too small, the measured values of  $R$  were considerably smaller than the corresponding values obtained when the gas contained a small proportion of water vapour. This decrease was due to the presence of free electrons, for which the factor  $k$  can clearly be considerably greater than unity when the ratio  $Z/p$  is not too small.‡

\* "Electricity in Gases," pp. 169-170.

† Haselfoot, *Proc. Roy. Soc., A*, **82**, p. 18 (1909), **87**, p. 350 (1912).

‡ Franck and Westphal, *Verh.d.D.Phys.Ges.*, **11**, pp. 146 and 176 (1909).

§ "Electricity in Gases," p. 160, and J. J. Thomson, "Conduction of Electricity through Gases," 1928, **1**, p. 90.

‡ See "Electricity in Gases," p. 175.

When the charged particles consist entirely of free electrons, as is the case in many dry gases†, the factor  $k$  can be determined by a method identical with that used to determine the quantity  $Ne$ .

Using a diffusion instrument similar to that shown in figure 1, the value of  $k$  corresponding to the given values of  $Z$  and  $p$  can be deduced from a single observation of the ratio  $R$ . For, knowing the normal distribution curve for the particular apparatus, the value of  $NeZ/k\pi$  can then be determined immediately; and as  $\pi = 1.013 \times 10^6$  dynes per square centimetre,  $Ne = 1.22 \times 10^{10}$  e.s.u., and  $Z$  is known, the factor  $k$  can be calculated. A useful relationship is

$$\frac{NeZ}{k\pi} = 40.3 \frac{Z}{k},$$

$Z$  being expressed in volts per centimetre.

Numerous experiments carried out by Townsend and his collaborators show that for a wide range of values of  $Z$  and  $p$  the factor  $k$  for electrons in a given gas depends only on the ratio of  $Z$  to  $p^*$ . This important property of the motion can be deduced from theoretical considerations. For, if  $Z$  and  $p$  were increased to  $\mu Z$  and  $\mu p$ , the mean distance between successive collisions would be decreased by the factor  $\mu$ , but the acceleration due to the electric force would be increased by the same factor; hence the mean energy acquired between collisions, and therefore the average effect of collisions, would be unaltered, so that it follows that the mean energy of the electrons would remain unchanged. It is, of course, assumed that a steady state exists under both sets of circumstances.

The root mean square velocity of the electrons, in centimetres per second, is given by

$$u = 1.15\sqrt{k} \times 10^7. \quad \dots\dots\dots(16)$$

A further useful relationship, giving the mean electronic energy  $\bar{E}$  in terms of electron-volts, is

$$\bar{E} = k/27.$$

It was found experimentally that  $k$  increases with  $Z/p$ ; and that, for a given value of  $Z/p$ ,  $k$  may vary considerably from gas

† Such gases are  $A$ ,  $Ne$ ,  $He$ ,  $N_2$ ,  $H_2$ ,  $CO$ ,  $CO_2$  and  $NO$ .

\* See *loc. cit.* p. 179.

to gas. Thus, the values of  $k$  in the rare gases were distinctly larger than the corresponding values in the active gases. These points are illustrated in the following table giving pairs of values of  $Z/p$  and  $k$  in argon and nitrogen\*. In this table,  $Z$  is expressed in volts per centimetre, and  $p$  in millimetres of mercury.

Table 1.

<i>A</i>		<i>N</i> <sub>2</sub>	
$Z/p$	$k$	$Z/p$	$k$
0.195	120	0.25	7.5
0.355	160	0.5	13.0
0.525	200	1	21.5
0.71	240	2	30.5
0.95	280	5	41.3
1.25	320	10	48.5
5	310	20	59.5
10	324	40	89
15	324	60	126

### 1.5—The Drift Velocity of Electrons.

The first accurate measurements of the drift velocity  $W$  of electrons moving through a gas under the action of a uniform electric field were made by Townsend. The apparatus used was similar to that shown in figure 1, except that the circular orifice  $S$  was replaced by a slit, and the composite electrode was of the form shown in figure 3. This electrode was placed so that  $C_2$  lay parallel to the slit, and symmetrically with regard to it.

As it is convenient to determine both the drift velocity and the mean energy of agitation in the same diffusion instrument, this form of the apparatus was also the one generally used to de-

\* See "Motion of Electrons in Gases," pp. 32 and 33.

termine  $k$ . In this case, the measurement consisted in determining the ratio  $R$  of the current arriving on  $C_2$  to the total current arriving on  $C_1$ ,  $C_2$  and  $C_3$ ; the normal distribution curve was given

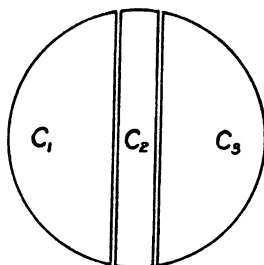


FIG. 3.

in a corresponding form. These currents are usually compared by means of an induction balance, a simple form of which is shown in figure 4; a more elaborate type is described in detail in §2.3.

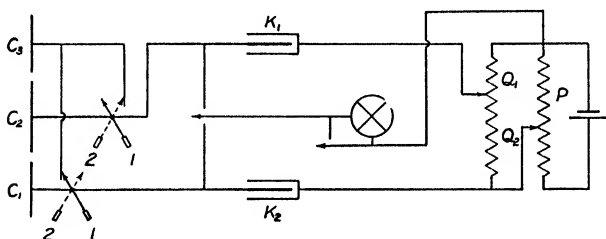


FIG. 4. A double-induction balance.

Switches are set in position (1) for determining  $k$ ;  $R = Q_1/(2Q_1 + Q_2)$ .  
 Switches are set in position (2) for determining  $W$ ;  $Q_2$  set to 0.

In order to determine  $W$ , the diffusion instrument was placed between two large, similar, vertical coils, so that the electrons could be made to move under the combined influence of a vertical electric field and horizontal magnetic field, the magnetic field being parallel to the slit and to  $C_2$ . When a current was passed through the coils, the electron stream was deflected as shown in figure 5,



the magnetic force here being assumed to be perpendicular to the plane of the paper.

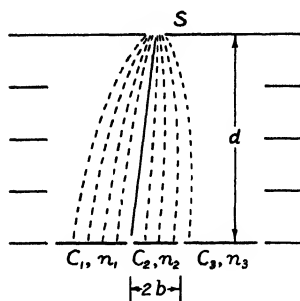


FIG. 5.

By measuring the angular deflection  $\theta$  of the stream, Townsend was able to calculate the drift velocity  $W$  by means of the formula

$$\tan \theta = \frac{HW}{Z}, \quad \dots\dots\dots (17)$$

$H$  being the magnetic force.

This equation was established as follows\* :

Let  $H$  lie along the  $y$ -axis, and the electric force  $Z$  along the  $z$ -axis. The equations for the motion of an electron between collisions then become

$$m \frac{d^2 x}{dt^2} = He \frac{dz}{dt},$$

and

$$m \frac{d^2 z}{dt^2} = Ze - He \frac{dx}{dt},$$

so that the velocities  $\dot{x}$  and  $\dot{z}$  are given by

$$\dot{x} = \frac{Z}{H} - A \cos (\omega t + \alpha)$$

and

$$z = A \sin (\omega t + \alpha),$$

\* Townsend, "Electricity in Gases," p. 100. See, also, Pidduck *Proc.Lond. Math.Soc.*, **15**, p. 123 (1915); L. G. H. Huxley, *Phil.Mag.*, **23**, p. 210 (1937), Townsend, *Phil.Mag.*, **25**, p. 459 (1938).

where  $\omega = He/m$ , the velocities at the beginning of a free path being  $Z/H - A \cos \alpha$  and  $A \sin \alpha$  respectively.

A collision between an electron and a molecule is—following the gas-kinetic theory—defined as an event in which, on the average, all directions of motion of the electron after the collision are equally probable; so that, if  $\dot{x}_1, \dot{x}_2, \dots, \dot{z}_1, \dot{z}_2, \dots$ , be the velocities after a number of consecutive collisions of an electron with molecules of the gas, the sums  $\dot{x}_1 + \dot{x}_2 + \dots, \dot{z}_1 + \dot{z}_2 + \dots$ , differ for different electrons and have an average value equal to zero for a large number of electrons. Hence, for a large number  $N$  of collisions involving a particular electron,

$$\Sigma A_1 \cos \alpha_1 = \frac{NZ}{H},$$

and

$$\Sigma A_1 \sin \alpha_1 = 0.$$

The distances  $x_1$  and  $z_1$  travelled along the axes of  $x$  and  $z$  in the first interval  $t_1$  are obtained by integrating the expressions for  $\dot{x}$  and  $\dot{z}$ :

$$x_1 = \frac{Z}{H}t_1 + \frac{A_1}{\omega} \left[ \sin \alpha_1 - \sin (\omega t_1 + \alpha_1) \right],$$

and

$$z_1 = \frac{A_1}{\omega} \left[ \cos \alpha_1 - \cos (\omega t_1 + \alpha_1) \right].$$

The distances traversed in the time  $NT = t_1 + t_2 + \dots + t_N$  are

$$\Sigma x_s = \frac{NZT}{H} - \frac{1}{\omega} \cdot \Sigma \left( \frac{Z}{H} - \dot{x}_s \right) \sin \omega t_s - \frac{1}{\omega} \cdot \Sigma z_s \cos \omega t_s,$$

and

$$\Sigma z_s = \frac{NZ}{H\omega} - \frac{1}{\omega} \cdot \Sigma \left( \frac{Z}{H} - \dot{x}_s \right) \cos \omega t_s + \frac{1}{\omega} \cdot \Sigma \dot{z}_s \sin \omega t_s.$$

The terms independent of  $Z$  vanish in estimating the mean displacements of a group of electrons starting from the origin, so that the velocities  $V_h$  and  $W_h$  along the axes of  $x$  and  $z$  are

$$V_h = \frac{\Sigma x_s}{NT} = \frac{Z}{H} \cdot \frac{\omega^2 T^2}{1 + \omega^2 T^2} = \frac{Ze}{m} \cdot \frac{\omega T^2}{1 + \omega^2 T^2}$$

and

$$W_h = \frac{\Sigma z_s}{NT} = \frac{Z}{H\omega T} \cdot \frac{\omega^2 T^2}{1 + \omega^2 T^2} = \frac{Ze}{m} \cdot \frac{T}{1 + \omega^2 T^2}.$$

When  $H$  is zero,  $\omega = 0$ , and  $W_h$  equals the drift velocity  $W$  in the absence of the magnetic field, so that  $W = ZeT/m$ .

The angle  $\theta$  is therefore given by

$$\tan \theta = \frac{V_h}{W_h} = \omega T = \frac{HW}{Z}. \quad \dots\dots\dots(17)$$

In practice, the magnetic force is adjusted until the current arriving on  $C_1$  is equal to the net current arriving on  $C_2$  and  $C_3$ , the centre of the stream then falling in the narrow gap between  $C_1$  and  $C_2$ . The deflection of the stream by the magnetic field is then given by  $\theta = \tan^{-1}(b/d)$ , where  $2b$  is the width of  $C_2$  and  $d$  is the distance between the plane of the slit and the plane of the collector electrodes. Under these circumstances, the drift velocity is given by

$$W = Zb/Hd.$$

It was found experimentally that, for any gas,  $W$  also depends only on the ratio of  $Z$  to  $p$ . This relationship, like that involving  $k$ , is to be expected on theoretical grounds.

For a given gas, the drift velocity, like  $k$ , increases with  $Z/p$ . Unlike  $k$ , however, the value of  $W$  for a given value of  $Z/p$  does not vary greatly from gas to gas. These points are illustrated by the results for carbon dioxide and hydrogen given in the following table.

Table 2.

$CO_2$		$H_2$	
$Z/p$	$W \times 10^{-5}$	$Z/p$	$W \times 10^{-5}$
0.25	1.2	0.25	6.5
0.5	2.5	0.5	9.0
1	5.5	1	11.9
2	11.8	2	16
5	50	5	25.5
10	108	10	38
20	138	20	70
50	195	50	217

As before,  $Z$  is expressed in volts per centimetre, and  $p$  in millimetres of mercury ;  $W$  is in centimetres per second.

### 1.6—The Mean Free Path of Electrons.

For charged particles moving in a gas under the action of a uniform electric field, there is a simple relation between the drift velocity  $W$ , the root mean square velocity  $u$  and the mean free path  $l$  ; this relation is

$$W = C. \frac{Ze l}{m u}, \dots\dots\dots (18)$$

where  $C$  is a numerical factor which depends on the velocity distribution and the variation of the mean free path with the velocity of agitation.

An equation of the form of (18) can be deduced immediately from the relation

$$W = \frac{Ze}{m} \cdot T$$

given in §1.5. Alternatively, suppose for simplicity that all the free paths are equal and that the velocities are all equal, and therefore equal to  $u$  ; then, neglecting the curvature of the paths, the average distance travelled in the direction of drift in the intervals  $l/u$  between collisions is given by

$$s = \frac{1}{2} \frac{Ze}{m} \cdot \left( \frac{l}{u} \right)^2,$$

as all directions of motion after a collision are equally probable, so that\*

$$W = s/(l/u) = \frac{1}{2} \cdot \frac{Ze l}{m u}.$$

Taking into account the distribution of free paths about the mean, but again neglecting the distribution of velocities, Townsend† obtained the result

$$W = \frac{Ze l}{m u}.$$

\* "Motion of Electrons in Gases," p. 16.

† "Electricity in Gases," pp. 82-84.

In order to allow for the velocity-distribution also, he used a general formula given by Langevin\* relating to the motion of ions in gases, and obtained a value of  $C$  equal to 0.815.

Equation (18) is discussed in more detail in Chapter 3, where it is shown that the formula generally used,

$$W = 0.815 \times \frac{Zel}{mu}, \dots\dots\dots(19)$$

is not likely to be in serious error.

For purposes of calculation, it is convenient to write equation (19) in the form

$$l = 8.10^{-9} \times W\sqrt{k}/Z,$$

or

$$L = 8.10^{-9} \times W\sqrt{k}/(Z/p), \dots\dots\dots(19a)$$

where  $L$  is the mean free path (in centimetres) at 1 millimetre pressure for the particular value of  $Z/p$  to which  $W$  and  $k$  refer. In these two formulae  $W$  is expressed in centimetres per second,  $Z$  in volts per centimetre, and  $p$  in millimetres of mercury.

It is clear from equation (19a) that  $L$ , like  $k$  and  $W$ , is a function of  $Z/p$ . In expressing experimental results it is customary to give  $L$  as a function of either the energy of agitation or the root mean square velocity of agitation.

Experimental determinations of  $L$  in various gases have brought to light the important fact that this quantity may vary considerably with  $u$ ; for example, in argon,  $L$  decreases by a factor 20 as  $u$  ranges from  $3.6 \times 10^7$  to  $19 \times 10^7$ . Each of the first gases investigated had a minimum value of  $L$  for some value of  $u$ , a phenomenon usually known as the Ramsauer effect; a number of gases investigated later, however, showed the opposite behaviour.

In general, the quantity  $L$  varies considerably from gas to gas, values as large as 1.6 cm being recorded for argon, and as low as  $4 \times 10^{-3}$  cm for carbon dioxide, as will be seen from the following table.

\* *Ann. de Chim. et de Phys*, **28**, p. 336 (1903).

Table 3\*.

<i>A</i>			<i>CO</i> <sub>2</sub>		
<i>k</i>	<i>u</i> × 10 <sup>-7</sup>	<i>L</i> × 10 <sup>2</sup>	<i>k</i>	<i>u</i> × 10 <sup>-7</sup>	<i>L</i> × 10 <sup>2</sup>
6	2.82	138	1.2	1.26	0.42
8	3.26	154	1.3	1.31	0.45
10	3.64	161	1.5	1.41	0.54
16	4.6	138	1.8	1.54	0.63
30	6.3	61.5	9	3.45	2.39
50	8.15	29.5	47	7.9	5.91
70	9.6	20.0	75	9.95	4.76
140	13.6	10.4	139	13.6	3.67

### 1.7—The Mean Energy lost by an Electron at a Collision.

In a steady state, the mean energy lost by an electron at a collision with a gas molecule is equal to the average work done on the electron between collisions by the electric field. It is found convenient to express this loss of energy in terms of  $\lambda$  the mean proportion of the average energy of an electron lost at a collision.

The coefficient  $\lambda$  is given by a formula of the type

$$\lambda = C_1 \cdot W^2/u^2, \quad \dots\dots\dots(20)$$

where  $C_1$ , like the factor  $C$ , is a number depending on the distribution of velocities about a mean, and on the variation of the free paths with the velocity of agitation.

An equation of the form of (20) can be derived as follows. Suppose, for simplicity, that the free paths are all equal, and that the electrons all have the same velocity of agitation  $u$ . Then, an electron moves a distance  $\delta$  counter to the field in the time  $\delta/W$ , making  $(u/l) \cdot (\delta/W)$  collisions during this period; so that  $\lambda$  is given by

$$(u/l) (\delta/W) \cdot \frac{1}{2} \lambda m u^2 = Ze\delta,$$

\* See "Motion of Electrons in Gases," pp. 34 and 35.

the right hand side representing the work done on the electron by the field. In §1.6 it was shown that, in the case at present under consideration,  $W$  is given by  $\frac{1}{2}Zel/mu$ . The above equation then becomes

$$\lambda = 4W^2/u^2.$$

In this work it has been customary to use for  $C_1$  the value 2.46 ( $=2/0.815$ ) given by Townsend\*. Equation (20) may then be written

$$\lambda = 2.46W^2/u^2. \quad \dots\dots\dots(21)$$

The coefficient  $\lambda$ , like  $L$ , can thus be calculated once  $W$  and  $k$  (or  $u$ ) have been determined. It is also clear that  $\lambda$  is a function of  $Z/p$  for any gas; usually, however, when expressing experimental results,  $\lambda$  is given as a function of  $u$ .

Pidduck† made a theoretical investigation of collisions between electrons and gas molecules, the latter being treated as imperfectly elastic spheres; he derived the formula

$$(k - f) + (1 - f)kM/m = W^2/\Omega^2,$$

where  $2f = (1 + \varepsilon)$ ,  $\varepsilon$  being the coefficient of restitution,  $M$  is the mass of a molecule, and  $\frac{1}{2}M\Omega^2$  the average energy of agitation of the molecules. By means of this formula, substituting values of  $W$  corresponding to  $k = 12$ , values of  $f$  are obtained equal to 0.9990 in air, 0.9990 in hydrogen, 0.9998 in nitrogen and 1.00001 in helium. From these results it may reasonably be concluded that, at low electronic energies, collisions between electrons and gas molecules are almost perfectly elastic. For elastic collisions, Pidduck's investigations led to a further formula,

$$\lambda = (2m/M) (1 - 1/k).$$

In the table below, values of  $\lambda$  calculated for *He* by means of this formula are compared with experimental values obtained by Townsend and Bailey‡, who used equation (21). The close agreement between the two sets of values in the region  $k < 80$  is good evidence that collisions in this gas are almost perfectly elastic for a wide range of values of  $k$ , and that equation (21) is reliable. The accuracy of this equation is discussed in further detail in Chapter 3.

\* "Motion of Electrons in Gases," p. 17.

† *Proc.Lond.Math.Soc.*, 15, p. 126 (1915).

‡ *Phil.Mag.*, 46, p. 657 (1923).

Table 4.  
*Energy Losses in Helium.*

$Z/p$	$k$	$(2m/M)(1 - 1/k)$	$(2.46W^2/u^2) \times 10^4$
0.013	1.77	1.19	1.3
0.02	2.12	1.45	1.56
0.05	3.68	1.99	2.3
0.20	11.3	2.48	2.55
1.0	53	2.68	2.4
1.5	79	2.70	2.6
2.5	124	2.72	3.4
5.0	172	2.73	9.8

Experimental results show that  $\lambda$  usually varies markedly with the electronic energy, and from gas to gas, being considerably less for the rare gases than for the active gases. The smallest value so far observed is for argon, and the largest for nitrous oxide, these values being  $1.5 \times 10^{-5}$  and  $1.5 \times 10^{-1}$  respectively.

Typical experimental results for the gases neon and carbon dioxide are given in the following table\*.

Table 5.

$Ne$		$CO_2$	
$k$	$\lambda \times 10^4$	$k$	$\lambda \times 10^4$
23.5	0.86	1.2	2.32
34.5	0.84	1.5	37.4
62	0.75	1.8	144
114	0.66	9	516
194	0.90	47	460
275	4.9	75	472
316	33	139	506

\* "Motion of Electrons in Gases," pp. 34 and 35.



## 1.8—Electrons in Gas Mixtures.

The experimental investigation of the motion of electrons through some gases is at times made difficult by certain properties of these gases; thus, in argon, it is not easy to investigate the behaviour of the electrons for low values of  $k$ , as the mean free path is very large and the energy loss at a collision very small.

In these cases it is often convenient to study a mixture of the gas with another gas for which the electronic properties are known. This method was used by Townsend and Bailey to complete the results for argon at low electronic energies; and more recently it has been used extensively at Sydney in the investigation of a number of gases having a high chemical activity.

Consider a mixture  $M$  containing the proportion  $f$  of the gas  $X$  which is to be investigated, and the proportion  $g$  ( $= 1 - f$ ) of a gas  $A$  whose properties are known. Let the quantities  $l$ ,  $L$  and  $\lambda$  in  $M$ ,  $X$  and  $A$ , for the same value of  $k$ , be denoted by the respective subscripts  $m$ ,  $x$  and  $a$ . Then, the average number of collisions made by an electron in moving 1 cm through the mixture is clearly  $1/l_m$ , and this must be equal to  $1/l_x + 1/l_a$ , so that we have

$$l_m^{-1} = l_x^{-1} + l_a^{-1},$$

or

$$L_m^{-1} = f.L_x^{-1} + g.L_a^{-1}. \quad \dots\dots\dots(22)$$

Further, in moving a distance 1 cm through the mixture, the average proportion of the mean energy lost by an electron in collisions is  $\lambda_m/l_m$ ; it is clear that this must equal the sum  $\lambda_x/l_x + \lambda_a/l_a$ . Accordingly, we have

$$\lambda_m.L_m^{-1} = f\lambda_x.L_x^{-1} + g\lambda_a.L_a^{-1}. \quad \dots\dots\dots(23)$$

Thus, knowing  $L_a$  and  $\lambda_a$ , and having determined  $L_m$  and  $\lambda_m$  as functions of  $k$  by the methods already outlined, the quantities  $L_x$  and  $\lambda_x$  can be calculated by means of equations (22) and (23).

Having obtained  $L_x$  and  $\lambda_x$  as functions of  $k$  (or  $u$ ), the corresponding values of the ratio  $(Z/p)_x$  and the drift velocity  $W_x$  can be derived from equations (19a) and (21) which may be written

$$Z/p = 4.4 \times 10^{-8} u^2 \lambda^{\frac{1}{2}}/L, \quad \dots\dots\dots(19a)$$

and

$$W = 0.64 u \lambda^{\frac{1}{2}}. \quad \dots\dots\dots(21)$$



## II

# THE MOTION OF ELECTRONS IN GASES IN WHICH NEGATIVE IONS ARE FORMED BY ATTACHMENT

### 2.1—The Probability of Attachment.

The methods of investigating the motion of electrons in gases described in Chapter I are inaccurate when there is present in the stream an appreciable proportion of negative ions. In this chapter an account is given of the methods developed by V. A. Bailey for the determination of  $k$ ,  $W$ ,  $L$  and  $\lambda$  when negative ions are present.

These methods also make possible the determination of  $h$  the probability of an electron's becoming attached to the molecule with which it collides. This quantity is introduced in the following manner. For a steady state in a uniform electric field in a gas at pressure  $p$ , the mean velocity of agitation  $\bar{U}$  and the drift velocity  $W$  are functions of  $Z/p$  only; in a large number  $N$  of collisions between electrons and gas molecules, a number  $hN$  result in attachment to form negative ions, where  $h$  is a number depending only upon the nature of the gas and the velocity  $\bar{U}$ .

In practice, the quantity most readily determined is the attachment coefficient  $\alpha$ , which is defined as the probability of an electron's becoming attached to a gas molecule in moving 1 cm in the direction of drift. The relation between  $h$  and  $\alpha$  is shown by the following considerations.

In moving a distance  $\delta$  in the direction of drift,  $N$  electrons made  $N\bar{U}\delta/lW$  collisions, as the average number of collisions made per second by an electron is  $\bar{U}/l$ —it being assumed that  $l$  does not vary appreciably with the velocity of agitation—and the time taken is  $\delta/W$ . Of these collisions a number  $h(N\bar{U}\delta/lW)$  will result in the formation of negative ions; but, from the definition of  $\alpha$ , this number must equal  $N\alpha\delta$ , so that

$$\alpha = h\bar{U}/lW. \quad \dots\dots\dots(24)$$

Equation (24) is not exact, as the variation of the mean free path with the velocity of agitation has been neglected, and the

assumption has been made that all electrons have the same velocity of drift. In general, however, the resulting error is not likely to be serious.

Experiments lead to values of  $u$ , not  $\bar{U}$ ; and it has been customary to use the equation

$$\alpha = hu/lW. \quad \dots\dots\dots(24a)$$

The additional error so introduced is again not likely to be of serious magnitude. Thus, for a Maxwellian distribution of velocities, which appears to be the broadest probable distribution, the ratio  $\bar{U}/u$  equals  $\sqrt{8/3\pi}$  ( $= 0.92$ ); so that, as the distribution which the bulk of evidence suggests as the most probable is somewhat narrower than a Maxwellian, the corresponding error is not likely to be greater than a few per cent.

## 2.2—The Energy of Agitation and the Attachment Coefficient.

In the present section, an account is given of the first method used by Bailey\* to obtain pairs of values of  $\alpha$  and  $k$ .

A schematic diagram of the diffusion instrument is shown in figure 6.

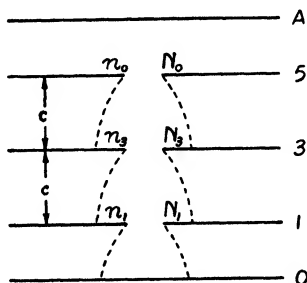


FIG. 6. Schematic diagram of Bailey's diffusion instrument.

Five parallel plates  $A$ ,  $5$ ,  $3$ ,  $1$ ,  $0$  and the guard rings  $4$  and  $2$  are maintained at suitable potentials so as to produce a uniform electric field; the distance  $c$  between  $5$  and  $3$  is equal to that between  $3$

\* *Phil. Mag.*, **50**, p. 825 (1925).

and 1; and the electrodes 5, 3 and 1 have slits of equal width which are accurately aligned, one above the other. Electrons are produced by illuminating the target *A* with ultra-violet light.

For this type of apparatus, the quantity *R* for either of the electrodes 1 and 3 is defined as the ratio of the electron current passing through the slit to that arriving at the plane of the electrode. As before, the normal distribution curve is obtained by solving the equation

$$\nabla^2 n = \frac{NeZ}{kT} \cdot \frac{\partial n}{\partial z}$$

for the particular boundary-conditions, and then integrating over the electrode. The solution of the above equation is in this case given in the form

$$q(x, z) = Az^{-\frac{1}{2}} \cdot \exp[-40.3 Zx^2/4kz],$$

where

$$q(x, z) = \int_{-\infty}^{\infty} n \cdot dy;$$

so that *R* is given by

$$\frac{\int_0^a q(x, c) \cdot dx}{\int_0^{\infty} q(x, c) \cdot dx},$$

where *2a* is the width of the slits\*. The ratio *R* is therefore a function of *Z/kc*:

$$R = R(Z/kc).$$

Let  $\xi$  be the ratio of the currents (composed of electrons and negative ions) received by 1 and 3 respectively, and  $\eta$  the corresponding ratio for 0 and 1. For electrode 3, let *S*<sub>3</sub> denote the ratio of the current passing through the slit to the current arriving at

\* The use of infinite limits in certain of the above integrals is justified, as the width of the slits and the length of the slit in 5 are so designed that, under the experimental conditions, appreciably all of the charged particles passing through 5 fall on the electrodes 0, 1 and 3.

the plane of this electrode; and let  $S_1$  be the corresponding ratio for electrode 1. Then, it is simply shown that

$$\left. \begin{aligned} S_3 &= \frac{\xi(1 + \eta)}{1 + \xi(1 + \eta)}, \\ \text{and} \\ S_1 &= \frac{\eta}{1 + \eta}. \end{aligned} \right\} \dots\dots\dots (25)$$

Let  $n_0$  be the number of electrons and  $N_0$  the number of ions passing per second through the slit in 5; and let  $n_3$ ,  $N_3$  and  $n_1$ ,  $N_1$  be the corresponding values for electrodes 3 and 1 respectively. Of the  $n_0$  electrons passing through 5, a number  $n_0 e^{-ac}$  arrive at the plane of 3\*, and these electrons have a distribution ratio  $R(Z/kc)$ , where  $R$  is a known function†. Hence

$$n_3 = an_0,$$

where

$$a = R(Z/kc).e^{-ac}.$$

Similarly,

$$n_1 = an_3 = a^2 n_0.$$

In the space between 5 and 3, the remaining  $n_0(1 - e^{-ac})$  electrons form ions, which arrive at the plane 3 with, say, a distribution ratio  $r$ . It follows that

$$\begin{aligned} N_3 &= N_0.R(Z/c) + n_0(1 - e^{-ac}).r \\ &= N_0.R + b.n_0, \text{ say.} \end{aligned}$$

Similarly,

$$\begin{aligned} N_1 &= N_3.R + b.n_3 \\ &= R^2 N_0 + (Rb + ba)n_0. \end{aligned}$$

It is also clear that

$$S_3 = (n_3 + N_3)/(n_0 + N_0)$$

\* For all the methods to be described, it is assumed that the ions formed by attachment are "permanent"; that is, that these ions do not dissociate before arriving at one or other of the collector electrodes.

† For negative ions which have moved a distance  $c$  in the direction of drift (that is, which have entered the particular chamber through the preceding slit), the distribution ratio is given by  $R(Z/c)$ , as  $k = 1$ . If no ions were present,  $R(Z/kc)$  would be equal to  $S_3$  (and  $S_1$ ).

and

$$S_3 S_1 = (n_1 + N_1)/(n_0 + N_0).$$

From these relations, the following equation is obtained:

$$a = S_3 (R - S_1)/(R - S_3). \quad \dots\dots\dots(26)$$

For given values of  $Z$  and  $p$ , the ratios  $\xi$  and  $\eta$  are measured, and  $S_3$  and  $S_1$  then obtained by means of equations (25). As  $Z/c$  is known, the distribution ratio  $R$  for ions can be read directly from the normal distribution curve. The value of  $a$  is then calculated by means of equation (26).

The relation

$$a = R(Z/kc).e^{-ac} \quad \dots\dots\dots(27a)$$

contains the two unknowns  $k$  and  $a$ . A second relation is obtained by determining the value of  $a_1$  corresponding to the same value of  $Z/p$ , but with  $Z$  and  $p$  altered to  $qZ$  and  $qp$  respectively. It is clear from equation (24a) in §2.1 that  $a/p$  is a function of  $Z/p$  alone; and  $k$  is also a function of  $Z/p$ . It follows that

$$a_1 = R(qZ/kc).e^{-qac}. \quad \dots\dots\dots(27b)$$

Thus, the values of  $k$  and  $a/p$  corresponding to a given value of  $Z/p$  can be determined from two sets of observations by means of equations (27a) and (27b).

Later, an apparatus was constructed in which the lengths of the two diffusion chambers could be varied\*. The computation of  $k$  and  $a$  is then simplified; two values of the quantity  $a$ , namely  $a$  and  $a_1$ , are determined, the first corresponding to  $Z$ ,  $p$  and  $c$ , the second to  $qZ$ ,  $qp$  and  $qc$ . As  $Z/p$  is unchanged,

$$a = R(Z/kc).e^{-ac}$$

and

$$a_1 = R(Z/kc).e^{-a^2 ac}.$$

It follows that

$$(q^2 - 1)ac = \log (a/a_1)$$

and

$$R(Z/kc) = a^{q^2/(q^2-1)}/a_1^{1/(q^2-1)},$$

whence  $a$  and  $k$  may be obtained.

\* V. A. Bailey and J. D. McGee, *Phil.Mag.*, 6, p. 1073 (1928).

### 2.3—The Experimental Determination of the Attachment Coefficient.

A more detailed description will now be given of the apparatus mentioned in the previous section, as it is essentially the same as that used in all the determinations of attachment coefficients described subsequently in this chapter.

The diffusion instrument is shown in figure 7.

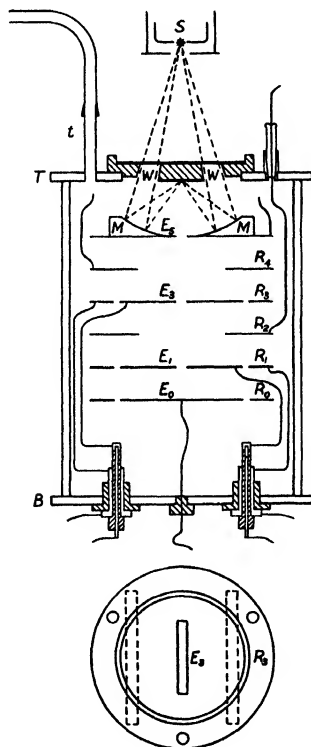


FIG. 7. Diagram of a diffusion instrument.

Three equi-spaced pillars standing on the brass base  $B$  support the guard rings  $R_0, R_1, R_2, R_3$  and  $R_4$  and the electrode  $E_s$ , distance pieces of glass tubing being used. Each of the electrodes  $E_0, E_1$  and  $E_3$  is supported by two strips of plate glass fixed to the corres-



ponding guard ring. Wires are connected to  $R_2$ ,  $R_4$  and  $E_5$  through capillary tubes mounted on the top plate  $T$ ; the leads connected to  $E_0$ ,  $E_1$  and  $E_3$  and the rings  $R_1$  and  $R_3$  are taken through ebonite plugs in the base  $B$ . Gas is admitted or withdrawn through the tube  $t$ ; in the more recent instruments this tube is connected to the base. Ultra-violet light from the spark  $S$  passes through an annular quartz window  $W$  and is reflected from the mirror  $M$  to the target  $A$  which serves as a source of photo-electrons. A uniform field is produced by applying suitable potentials to the electrodes and guard rings. The electrodes  $E_1$ ,  $E_3$  and  $E_5$  consist of rings over which silver foil is tightly stretched. In each case the slit cut in the foil is 4 mm wide. The three slits are parallel and are arranged one above the other, those in  $E_1$  and  $E_3$  being considerably longer than that in  $E_5$ , so that their length can be regarded as infinite in the computation of the distribution function  $R$ . The distance between successive rings is 2 cm, and  $c$  is 4 cm.

The very small currents arriving at the electrodes ( $\sim 10^{-12}$  amp) are compared by a null method, an elaboration of Townsend's induction-balance being used (see figure 8). This method has the

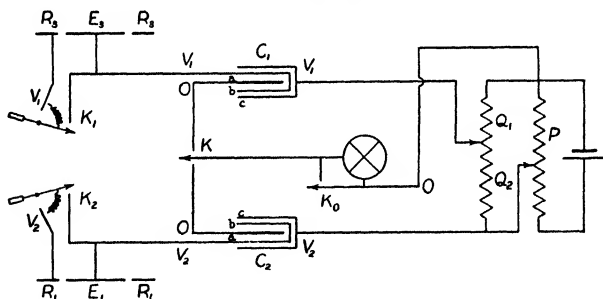


FIG. 8. Apparatus used to compare the small electric currents in the diffusion instrument.

important advantage that, during an observation, the electrostatic conditions within the instrument remain undisturbed. Each of the double condensers  $C_1$  and  $C_2$  consists essentially of three concentric brass cylinders  $a$ ,  $b$  and  $c$ , insulated from one another by means of ebonite rings. The electrode  $E_1$  is connected to the cylinder  $b_1$ ; by means of the key  $K_1$ ,  $E_1$  can be brought to the potential  $V_1$  of its guard ring  $R_1$  and then left insulated at that

potential. Similarly,  $E_2$  is connected to  $b_2$  and can be left insulated at the potential  $V_2$ . The cylinders  $a_1$  and  $a_2$  can be connected in turn to an electrometer by means of the key  $K$ , and all three— $a_1$ ,  $a_2$  and the electrometer—can be brought to zero potential with the earthing key  $K_0$ . By means of the resistance boxes  $Q_1$  and  $Q_2$  and the sliding potentiometer  $P$ , the outer cylinders  $c_1$  and  $c_2$  can be brought to any desired potentials  $v_1$  and  $v_2$ . Initially, let  $a_1$ ,  $a_2$  and the electrometer be insulated at zero potential; let the electrodes  $E_1$  and  $E_2$  with their attached cylinders be insulated at potentials  $V_1$  and  $V_2$  respectively; and let  $v_1 = v_2 = 0$ . When charges  $q_1$  and  $q_2$  arrive on  $E_1$  and  $E_2$  respectively, the potentiometer and resistances can be adjusted so as to restore the potentials of all the insulated systems to their original values, provided the cylinders  $c$  are well screened from the cylinders  $a$ .

From the initial and final conditions of the system attached to  $E_1$  we obtain the equation

$$q_1 = v_1 \cdot C_{1bc},$$

where  $C_{1bc}$  is the capacity of the condenser formed by the cylinders  $b_1$  and  $c_1$ . Similarly,

$$q_2 = v_2 \cdot C_{2bc}.$$

If the condensers are identical,  $C_{1bc}$  equals  $C_{2bc}$ ; so that

$$q_1/q_2 = v_1/v_2 = Q_1/(Q_1 + Q_2).$$

In this way the ratios  $\xi$  and  $\eta$  can be determined experimentally.

The distribution ratio  $R$  was calculated in a manner similar to that used for earlier apparatus\*. In order to verify these calculations, experiments were carried out in hydrogen, for which the values of  $k$  are known. It was found that, for  $R > 0.36$ , the experimental values of  $S_1$  agreed closely with the calculated values of  $R$ ; as  $R$  decreased below this value, however, the difference between  $S_1$  and  $R$  became greater. This behaviour when the stream diverged strongly was due principally to the effect of the ends of the slit. The values of  $S_3$  were found to be consistently about 6% less than those of  $S_1$ . It was decided that this difference was due partly to a lack of uniformity in the top field and partly to slight errors in the dimensions and location of the slits.

\* *Phil. Mag.*, **50**, p. 825 (1925).

These results led to the conclusion that two distribution curves are required, one for each of the electrodes 3 and 1: for the latter electrode the distribution ratio  $R''$  was taken equal to the calculated values for  $R > 0.40$  and equal to the experimental values of  $S_1$  for smaller values of  $R$ ; the ratio  $R'$  for electrode 3 was taken equal to  $0.94R''$ .

A slight modification of the theory of the method given in §2.2 is thus necessary; however, it can be shown that, if a quantity  $\alpha''$  be introduced, where

$$\alpha'' = R''(Z/kc)e^{-\alpha c},$$

it is related to the experimentally determined ratios  $S_3$  and  $S_1$  by the equation

$$\alpha'' = S_3(R'' - S_1)/(R' - S_3).$$

The experimental procedure for determining  $\alpha$  and  $k$  is thus unaltered.

This method was first applied to dry air. It was found that the values obtained for  $k$  were in satisfactory agreement with those given previously by Townsend and Tizard. As  $Z/p$  was varied from 0.422 to 0.250, the values of  $\alpha/p$  varied from  $3.36 \times 10^{-3}$  to  $0.54 \times 10^{-3}$ . Corresponding values of  $h$  were calculated by using the results for  $W$  given by Townsend and Tizard and substituting in the formula

$$h = 7 \times 10^{-16} \alpha W^2/Z, \quad \dots\dots\dots(28)$$

which is obtained by eliminating  $u/l$  from the equations  $\alpha = hu/lW$  and  $W = 0.815Zel/mu$ , and then expressing  $Z$  in volts per centimetre. In this way the typical results shown in the following table were obtained for air.

Table 6.

$Z/p$	$u \times 10^{-7}$	$h \times 10^6$
0.5	3.3	3.3
1.0	4.5	2.0
2.0	6.0	0.7

It should be noted that this method makes possible only the determination of  $k$  and  $\alpha$ . However, knowing  $k$  and  $\alpha/p$  and one of the three quantities  $W$ ,  $L$  and  $\lambda$  for a given range of  $Z/p$ , it is clear that the corresponding values of the remaining two, and of the probability  $h$ , can be obtained. In the above case it was found convenient to use values of  $W$  obtained previously by Townsend and Tizard.

The same apparatus was used later for some experiments with hydrogen chloride and ammonia\*. The variation of  $k$  and  $\alpha/p$  with  $Z/p$  was investigated in the manner described above. It was found that the  $(Z/p, k)$  curve for  $HCl$  lay considerably below that of all other gases investigated previously.

Rough estimates were made of  $\lambda$  and  $h$  by means of the formulae†

$$\lambda = 305 L^2(Z/p)^2/k^2,$$

and

$$h = 11.1 (\alpha/p)L^2(Z/p)/k,$$

the values of  $L$  being derived from viscosity measurements. These results showed that the probability  $h$  was large in both gases, ( $\sim 10^{-5}$  to  $10^{-3}$ ), and that large values of  $\lambda$  occurred in  $HCl$ . The results for  $NH_3$  were not satisfactory; it was decided that the  $NH_3$  contained a proportion of  $H_2$  which was slowly increasing with time.

The unsatisfactory results for  $NH_3$  led to the design of the instrument in which the inter-electrode distance  $c$  could be varied. As mentioned in §2.2, the calculation of  $\alpha$  and  $k$  from the observations made with this instrument is very simple. Tests were made in hydrogen, the values of  $S_3$  and  $S_1$  agreeing well with calculated values of  $R$  greater than 0.5. Experiments were carried out on  $NH_3$ ; curves were obtained showing the variation with  $Z/p$  of  $k$  and  $\alpha/p$ , the consistency of the results deduced from observations of  $\xi$  and  $\eta$  for various combinations of  $Z$ ,  $p$  and  $c$  being good evidence that the method was reliable. It was shown that, as  $k$  increased from 5.5 to 64, the probability  $h$  increased by a factor of

\* V. A. Bailey and A. J. Higgs, *Phil. Mag.*, 7, p. 277 (1929).

† The first relation is obtained by eliminating  $W$  from  $\lambda = 2.46W^2/u^2$  and  $W = 0.815 \text{ Zel}/mu$ ; the second by eliminating  $W$  from  $\alpha = hu/lW$  and  $W = 0.815 \text{ Zel}/mu$ . In both cases  $u$  is replaced by  $1.15\sqrt{k} \times 10^7$ , and then  $Z$  expressed in volts per centimetre and  $p$  in millimetres of mercury.

about 14; and that, as  $k$  increased from 5.5 to 45, the quantity  $L$  increased by a factor of about 1.8.

A further investigation, using the original instrument shown in figure 7, was carried out by McGee and Jaeger\*. The gas selected was pentane; some time previously, when studying ionic mobilities, E. M. Wellish had noticed an "ageing" effect in this gas†. For values of  $Z/p$  ranging from 0.60 to 40, the quantities  $k$  and  $a/p$  were calculated in a manner similar to that used by Bailey for air. In order to estimate  $L$ ,  $\lambda$  and  $h$ , approximate values of  $W$  were obtained by means of a Townsend diffusion apparatus (see §1.5). It was found that  $\lambda$  has a maximum value  $5.4 \times 10^{-2}$  at  $u = 2.4 \times 10^7$ , falling to  $1.0 \times 10^{-2}$  at  $u = 10.0 \times 10^7$ ; that  $L$  has a maximum of  $2.7 \times 10^{-2}$  at  $u = 2.7 \times 10^7$ ; and that the probability  $h$  diminishes from  $1.35 \times 10^{-5}$  to  $0.15 \times 10^{-5}$  as  $u$  increases from  $1.9 \times 10^7$  to  $5.5 \times 10^7$ .

## 2.4—The Magnetic Method for the Determination of the Drift Velocity.

The methods outlined so far in this book make possible the determination of  $k$ ,  $\lambda$ ,  $L$  and  $W$  in the absence of negative ions, and of  $k$  and  $a/p$  when negative ions are present. In this section, a description is given of a method devised by Bailey‡ for determining  $W$ —and thence  $\lambda$ ,  $L$  and  $h$ —in gases in which negative ions are formed.

This method depends upon the fact that, when a magnetic field  $H$  is applied parallel to the electric field, the divergence of the stream of electrons is reduced.

Townsend has shown§ that, in the presence of a magnetic field lying along the axis of  $z$ , the coefficients of diffusion in the direction of the axes are given by

$$K_x = K_y = \frac{K}{1 + \omega^2 T^2}$$

and

$$K_z = K,$$

\* *Phil. Mag.*, **6**, p. 1107 (1928).

† *Phil. Trans.*, A, **209**, p. 249 (1909).

‡ *Phil. Mag.*, **9**, pp. 560 and 625 (1930).

§ "Electricity in Gases," p. 100; see, also, Huxley, *Phil. Mag.*, **23**, p. 217 (1937).

where  $\omega = He/m$ ,  $T$  is the mean time between collisions and  $K$  is the ordinary coefficient of diffusion satisfying the relation

$$\frac{W}{K} = \frac{NeZ}{k\Pi}.$$

It was also shown that, for given values of  $Z$  and  $p$ , the drift velocity  $W$  in the direction of  $Z$  is not affected by the presence of the magnetic field; and (see §1.5) that

$$\omega T = \frac{HW}{Z}.$$

The equations of motion then become

$$nV_x = -K_x \frac{\partial n}{\partial x},$$

$$nV_y = -K_y \frac{\partial n}{\partial y},$$

$$nV_z = -K_z \frac{\partial n}{\partial z} + nW;$$

so that, from the equation of continuity, assuming a steady current, we obtain

$$\frac{1}{\Phi} \left( \frac{\partial^2 n}{\partial x^2} + \frac{\partial^2 n}{\partial y^2} \right) + \frac{\partial^2 n}{\partial z^2} = \frac{W}{K} \cdot \frac{\partial n}{\partial z}, \quad \dots\dots(29)$$

where

$$\Phi = 1 + \left( \frac{HW}{Z} \right)^2, \quad \dots\dots\dots(30)$$

$Z$  being expressed in e.m.u. and  $H$  in gauss.

Pidduck\* obtained for  $nV_x$  and  $nV_y$  the respective expressions

$$-K \frac{\frac{\partial n}{\partial x} + \omega T \frac{\partial n}{\partial y}}{1 + \omega^2 T^2} \text{ and } -K \frac{-\omega T \frac{\partial n}{\partial x} + \frac{\partial n}{\partial y}}{1 + \omega^2 T^2};$$

it is clear, however, that the differential equation obtained for  $n$  when these expressions are used is identical with (29).

\* *Proc. Lond. Math. Soc.*, 15, p. 125 (1915).

Equation (29) can be simplified by integrating each term with respect to  $y$  (the  $y$ -axis being taken parallel to the slits): for, as  $n$  and hence  $\frac{\partial n}{\partial y}$  are appreciably equal to zero at the side boundary, we then obtain

$$\frac{1}{\Phi} \frac{\partial^2 q}{\partial x^2} + \frac{\partial^2 q}{\partial z^2} = \frac{W}{K} \cdot \frac{\partial q}{\partial z},$$

where  $q = \int_{-\infty}^{\infty} n \cdot dy$ . Then, using the relation  $\frac{W}{K} = 40.3 \frac{Z}{k}$ , and

replacing  $z$  by  $c\xi$ , this equation becomes

$$\frac{\partial^2 q}{\partial x^2} = 40.3 \frac{Z\Phi}{kc} \cdot \frac{\partial q}{\partial \xi} - \frac{\Phi}{c^2} \cdot \frac{\partial^2 q}{\partial \xi^2}.$$

If  $Z/kc$  is not too small, the second term on the right can be neglected in comparison with the first, so that we may write

$$\frac{\partial^2 q}{\partial x^2} = 40.3 \frac{Z\Phi}{kc} \cdot \frac{\partial q}{\partial \xi}.$$

In this case, therefore, the distribution ratio  $R$  must be a function of  $Z\Phi/kc$ . As  $H$  tends to zero,  $\Phi$  approaches the value 1, so that  $Z\Phi/kc$  approaches  $Z/kc$ ; hence it will be seen that the new distribution ratio is obtained by replacing the variable  $Z/kc$  by  $Z\Phi/kc$ .

Several methods of obtaining  $W$  from observations made with parallel electric and magnetic fields have been given by Bailey. Of these, the most convenient procedure is that described below; this method will be referred to as the magnetic method.

First, the quantities  $k$  and  $a$  are determined by the method outlined in §2.2\*. The magnetic field is then adjusted until the divergence of the stream is the same as that of a stream composed entirely of negative ions, that is until  $S_1$  (and  $S_2$ ) is equal to  $R(Z/c)$ . Let this value of the magnetic force be denoted by  $H_0$  and the corresponding value of  $\Phi$  by  $\Phi_0$ . Then,

$$R(Z\Phi_0/kc) = R(Z/c),$$

so that we have

$$k = \Phi_0 = 1 + (H_0 W/Z)^2,$$

\* Hereafter, this method will be referred to as the original method.

whence

$$W = \frac{Z}{H_0} \sqrt{k - 1} \times 10^8, \quad \dots\dots\dots(31)$$

$Z$  now being expressed in volts per centimetre.

The above derivation of this formula for  $W$  is not strictly accurate, but it will be shown later that the correct expression for  $W$  requires merely the introduction of a factor which is not likely to differ greatly from unity. The close agreement between the values of  $W$  obtained by this method and those obtained by Townsend's method is shown by the results for hydrogen given in the table below; this agreement is good evidence that equation (31) is reliable.

Table 7

$$c = 4 \text{ cm}, Z = 4 \text{ V/cm}, R(Z/c) = 0.555.$$

$Z/p$	$k$	$p$	$H_0$	$W_M \times 10^{-6}$	$W_T \times 10^{-6}$
0.625	6.5	6.4	950	0.99	0.99
5	26	0.8	760	2.63	2.55
20	78	0.2	500	7.02	7.0
$W_M$ calculated from (31); $W_T$ denotes Townsend's values.					

It will be seen that, by this method, accurate determinations of  $W$  can be made even when a large proportion of negative ions is present within the gas.

A simple formula for deriving  $\lambda$  from  $k$  and  $H_0/Z$  is obtained by eliminating  $W$  and  $u$  from

$$\lambda = 2.46 W^2/u^2, u = 1.15 \sqrt{k} \times 10^7, \text{ and } W = \frac{Z}{H_0} \sqrt{k - 1} \times 10^8.$$

This relation is

$$\lambda = 186 (Z/H_0)^2 (1 - 1/k). \quad \dots\dots\dots(32)$$

When  $k$  is sufficiently large, this equation may be written

$$\lambda = 186 (Z/H_0)^2.$$



The curve  $(Z/p, \lambda)$  can thus be determined over a wide range of values of  $Z/p$  from observations of  $H_0$  alone.

The mean free path is derived most conveniently by means of the equation

$$L = 8 \times 10^{-9} W \sqrt{k} / (Z/p),$$

and probabilities of attachment by the formula

$$h = 7 \times 10^{-16} a W^2 / Z.$$

The original method and the magnetic method together afford a powerful means for investigating the behaviour of electrons in gases in which negative ions are formed by attachment.

In this manner, a study of the motion of electrons was made in ammonia, water vapour and hydrogen chloride\*. Initial experiments made with ammonia yielded values of  $k$  and  $a/p$  which were in good agreement with those obtained earlier by Bailey and McGee. Observations of  $H_0$  were then made in the same gas. A number of experiments were performed in order to check the theory, and these verified that  $H_0/Z$  is a function of  $Z/p$  and that  $S_3 = R$  when  $H$  is such that  $S_1 = R$ .

Curves for each of the three gases were given, showing the variation with  $Z/p$  of the quantities  $k$ ,  $a/p$  and  $W$ , and the variation with  $u$  of the quantities  $L$ ,  $\lambda$  and  $h$ . It was pointed out that a comparison could be drawn between the light-absorption curve of a gas and the curve  $(\lambda, u)$ . The comparison is made by setting  $\hbar\nu$  equal to  $mu^2/2$ , where  $\hbar$  is Planck's constant and  $\nu$  is the frequency of the light; and it was shown that large values of  $\lambda$  correspond to strong absorption bands and low values of  $\lambda$  to regions of small light-absorption. It was also suggested that the probability of an electron's becoming attached to a molecule is the greater the farther the electron penetrates into the molecule; and that, in the gases  $NH_3$ ,  $H_2O$  and  $HCl$ , it is probable that no negative ions are formed at low values of  $Z/p$ . Further, these experiments showed conclusively that  $h$  can vary considerably with the electronic energy; in  $NH_3$ , for example,  $h$  varies by a factor of at least one hundred.

The next gas investigated was nitrous oxide†. It was found that more-accurate results were obtained by keeping the inter-

\* V. A. Bailey and W. E. Duncanson, *Phil.Mag.*, **10**, p. 145 (1930).

† V. A. Bailey and J. B. Rudd, *Phil.Mag.*, **14**, p. 1033 (1932).

electrode distance  $c$  at its maximum value 4 cm. The original method could have been used, but the following means of obtaining  $a$  and  $k$  proved more convenient.

Observations were made to determine the value of the quantity  $a$ , first with the magnetic field equal to zero and then equal to  $H_0/2$ ; let these two values be denoted by  $a$  and  $a_m$  respectively. Then,

$$a = R(Z/kc).e^{-ac}$$

and

$$a_m = R(Z\Phi/kc).e^{-ac},$$

where

$$\Phi - 1 = (H_0 W/Z)^2/4.$$

However, it has been shown that

$$k - 1 = (H_0 W/Z)^2,$$

so that we have

$$(\Phi - 1)/(k - 1) = 1/4.$$

From these relations, the following equation, giving  $k$ , can be obtained :

$$\log \left[ R \left( Z \cdot \frac{k+3}{4kc} \right) \right] - \log \left[ R(Z/kc) \right] = \log a_m - \log a.$$

For given values of  $Z$  and  $c$ , the left side is a known function of  $k$  which can be conveniently represented by a curve. In practice,  $c$  was fixed at 4 cm, and values of  $Z$  of 8, 12, 16 and 24 V/cm were used; four curves were thus necessary. The values of  $a$  and  $a_m$  were determined experimentally and the value of  $k$  then obtained by means of the appropriate curve. The corresponding value of  $a$  was calculated from the relation:  $a = R(Z/kc)e^{-ac}$ . Knowing the three curves  $(Z/p, k)$ ,  $(Z/p, a/p)$  and  $(Z/p, H_0/Z)$ , the quantities  $W$ ,  $\lambda$ ,  $L$  and  $h$  were derived by means of equations given earlier in this section. The values obtained for  $k$  and  $W$  were in fair agreement with those given by Skinker and White, whose observations were made at low values of  $Z/p$  where  $h$  is negligible; also in agreement with Skinker and White, it was found that ionization by attachment becomes appreciable at values of  $Z/p$  greater than 2. The curves  $(L, u)$  and  $(\lambda, u)$  for  $N_2O$  were found to be very similar to the corresponding curves for  $CO_2$ . In both gases the maximum

in the  $(\lambda, u)$  curve is closely matched with the most pronounced peak in the light-absorption curve. The maximum value of  $\lambda$  observed in  $N_2O$ , namely 15.5 per cent., is remarkably high.

Nitric oxide\* was investigated in the same manner as nitrous oxide. The values obtained for  $k$  and  $W$  were also in good agreement with those given earlier by Skinner and White†. Curves were given showing the variation with  $u$  of  $L$  and  $\lambda$ . In this case the maximum in the  $\lambda$  curve does not correspond to the fundamental vibration-absorption band, but lies close to the second harmonic of this band. Accurate determinations of  $h$  were not possible; however, it was found that  $h$ , like  $\lambda$ , diminishes notably as  $u$  increases, this conclusion being in agreement with that reached by Skinner and White.

## 2.5—The Method of Mixtures.

In §1.8 it was pointed out that the experimental investigation of the motion of electrons in a gas is at times somewhat difficult on account of certain properties of this gas; and that in such cases it is often convenient to study a mixture of the gas with another gas for which the relevant electronic properties are known.

When negative ions are formed in the mixture, the values of  $L$  and  $\lambda$  can be determined by the methods described previously in this chapter; so that the quantities  $L$ ,  $\lambda$ ,  $Z/p$  and  $W$  for the pure gas can be determined as functions of  $k$  by means of equations (22), (23), (19a) and (21).

The probability of attachment and the attachment coefficient can readily be obtained from values of  $a$  for the mixture; for, by an argument similar to that used in the derivation of equation (24a), it can be shown that

$$(a/p)_m = (h_x f/L_x + h_a g/L_a) (u_m/W_m), \dots\dots(24b)$$

the notation corresponding to that used in §1.8. The probability  $h_x$  can be obtained by means of this equation, whence  $(a/p)_x$  can be calculated from equation (24a).

A more powerful method, however, is the following‡. Two mixtures are prepared; the first contains the proportion  $f_1$  of

\* V. A. Bailey and J. M. Somerville, *Phil.Mag.*, **17**, p. 1169 (1934).

† M. F. Skinner and J. V. White, *Phil.Mag.*, **46**, p. 630 (1923).

‡ V. A. Bailey and R. H. Healey, *Phil.Mag.*, **19**, p. 725 (1935).

the gas  $X$  whose properties are to be determined and the proportion  $g_1 (= 1 - f_1)$  of a gas  $A$  of known electronic properties; in the second mixture, consisting of the gas  $X$  and a known gas  $B$ , these proportions are denoted by the subscript 2. For a given value of  $k$  let  $(L_1, \lambda_1)$  and  $(L_2, \lambda_2)$  be the values of  $(L, \lambda)$  in mixtures 1 and 2 respectively, and for the same value of  $k$  let  $(L_x, \lambda_x)$ ,  $(L_a, \lambda_a)$  and  $(L_b, \lambda_b)$  be the corresponding values of  $(L, \lambda)$  in the respective gases  $X$ ,  $A$  and  $B$ .

Then, as shown in §1.8,

$$\left. \begin{aligned} L_1^{-1} &= f_1 L_x^{-1} + g_1 L_a^{-1}, \\ L_2^{-1} &= f_2 L_x^{-1} + g_2 L_b^{-1}, \end{aligned} \right\} \dots\dots\dots (33)$$

and

$$\left. \begin{aligned} \lambda_1 L_1^{-1} &= f_1 \lambda_x L_x^{-1} + g_1 \lambda_a L_a^{-1}, \\ \lambda_2 L_2^{-1} &= f_2 \lambda_x L_x^{-1} + g_2 \lambda_b L_b^{-1}. \end{aligned} \right\} \dots\dots\dots (34)$$

It is convenient to introduce the quantities  $\varrho_1$ ,  $\varrho_2$ ,  $q_a$ ,  $q_b$ ,  $r_a$ ,  $r_b$ ,  $s$  and  $t$  defined by the equations

$$\left. \begin{aligned} \varrho_1 &= f_1^{-1} - 1, & \varrho_2 &= f_2^{-1} - 1, \\ q_a &= \varrho_1 L_a^{-1}, & q_b &= \varrho_2 L_b^{-1}, \\ r_a &= \varrho_1 \lambda_a L_a^{-1}, & r_b &= \varrho_2 \lambda_b L_b^{-1}, \\ s &= L^{-1}, & t &= \lambda L^{-1}. \end{aligned} \right\} \dots\dots (35)$$

From the relationships  $\lambda = 2.46 W^2/u^2$ ,  $L = 8 \times 10^{-9} W \sqrt{k}/(Z/p)$  and  $u = 1.15 \sqrt{k} \times 10^7$ , it is easily shown that

$$\left. \begin{aligned} s &= 17k^{-1}(Z/p)\lambda^{-1}, \\ t &= 17k^{-1}(Z/p)\lambda^{\frac{1}{2}}. \end{aligned} \right\} \dots\dots (36)$$

Then, using the quantities defined above, equations (33) and (34) become

$$\left. \begin{aligned} s_1 f_1^{-1} &= q_a + L_x^{-1}, \\ s_2 f_2^{-1} &= q_b + L_x^{-1}, \end{aligned} \right\} \dots\dots (37)$$

and

$$\left. \begin{aligned} t_1 f_1^{-1} &= r_a + \lambda_x L_x^{-1}, \\ t_2 f_2^{-1} &= r_b + \lambda_x L_x^{-1}. \end{aligned} \right\} \dots\dots\dots (38)$$

Eliminating  $L_x^{-1}$  from equations (37), and  $\lambda_x L_x^{-1}$  from (38), the following equations are obtained :

$$q_a - q_b = s_1 f_1^{-1} - s_2 f_2^{-1}, \quad \dots\dots\dots (39)$$

$$r_a - r_b = t_1 f_1^{-1} - t_2 f_2^{-1}. \quad \dots\dots\dots (40)$$

The manner in which  $s$  and  $t$  are related to the observed quantity  $H_0$  is now shown. From the relation

$$\lambda = 186 (Z/H_0)^2 (1 - 1/k)$$

and the equations (36), it follows that

$$s f^{-1} = k^{-1} (1 - 1/k)^{-\frac{1}{2}} \sigma \quad \dots\dots\dots (41)$$

and

$$t f^{-1} = k^{-1} (1 - 1/k)^{\frac{1}{2}} \tau, \quad \dots\dots\dots (42)$$

where

$$\sigma = 1.25 f^{-1} H_0/p, \quad \dots\dots\dots (43)$$

and

$$\tau = 231 f^{-1} Z^2/pH_0. \quad \dots\dots\dots (44)$$

Equations (39) and (40) may thus be written in the simple forms

$$x = \sigma_1 - \sigma_2, \quad \dots\dots\dots (45)$$

$$y = \tau_1 - \tau_2, \quad \dots\dots\dots (46)$$

where

$$x = k(1 - 1/k)^{\frac{1}{2}}(q_a - q_b), \quad \dots\dots\dots (47)$$

and

$$y = k(1 - 1/k)^{-\frac{1}{2}}(r_a - r_b). \quad \dots\dots\dots (48)$$

In equations (45) and (46), the quantities  $x$  and  $y$  are known in terms of  $k$ , the quantities  $\sigma_1$  and  $\tau_1$  in terms of  $(Z/p)_1$  and the quantities  $\sigma_2$  and  $\tau_2$  in terms of  $(Z/p)_2$ . For a given value of  $(Z/p)$  we may therefore regard equations (45) and (46) as a pair of simultaneous equations in  $k$  and  $(Z/p)_1$ .

The solution can be obtained by trial-and-error methods. A simple, graphical method of solution, which has proved particularly convenient, is described below.

The values of  $L_a$ ,  $\lambda_a$ , and  $L_b$ ,  $\lambda_b$  are known functions of  $k$  from the data for gases  $A$  and  $B$  respectively; thence, by using equation (35), the values of  $q_a$ ,  $r_a$ ,  $q_b$  and  $r_b$  are obtained as functions of  $k$ ; the corresponding values of  $x$  and  $y$  are then calculated by means of equations (47) and (48). The  $(x, y)$  curve is drawn on transparent paper, and the  $(x, k)$  or  $(y, k)$  curve on ordinary graph paper. From the experimentally-determined curves  $(Z/p, H_0/Z)$  for each mixture, the corresponding quantities  $\sigma$  and  $\tau$  are obtained as functions of  $Z/p$  by means of equations (43) and (44); the curves  $(\sigma, \tau)$ —denoted by the symbols I and II—are then drawn to the same scale as the  $(x, y)$  curve,  $x$  and  $\sigma$  being corresponding co-ordinates.

The  $(x, y)$  curve, drawn on transparent paper, is placed over the sheet on which the two  $(\sigma, \tau)$  curves are drawn, in such a manner that the corresponding axes are parallel, the origin lying at a selected point on II. The point of intersection of the curve  $(x, y)$  with I determines a value of  $(Z/p)_1$  corresponding to the value  $(Z/p)_2$  determined by the initial point taken on II; also, this point of intersection determines a value of  $x$ —or  $y$ —and thence from the curve  $(x, k)$ —or  $(y, k)$ —the corresponding value of  $k$ . Thus, by sliding the origin of the  $(x, y)$  curve along II, the curves  $(Z/p, k)$  for mixtures 1 and 2 can be rapidly obtained.

Knowing the curves  $(Z/p, k)$  and  $(Z/p, H_0/Z)$  for each mixture, the curves  $(L, u)$  and  $(\lambda, u)$  for the gas  $X$  can be readily derived; for, from these known curves, the quantities  $s$  and  $t$  for each mixture can be obtained as functions of  $k$ , and the values of  $L_x$  and  $\lambda_x$  then calculated by means of the first of equations (37) and (38) which may be written in the forms

$$L_x = 1/(s_1 g_1^{-1} - q_a), \quad \dots \dots \dots (49)$$

and

$$\lambda_x = (t_1 g_1^{-1} - r_a)/(s_1 g_1^{-1} - q_a). \quad \dots \dots \dots (50)$$

From these results, the  $(Z/p, k)$  curve for the gas  $X$  can be obtained by means of equation (36),

$$Z/p = k\lambda^{\frac{1}{2}}/17L.$$

Finally, the  $(Z/p, W)$  curve for the gas  $X$  is obtained from the relations  $\lambda = 2.46W^2/u^2$  and  $u = 1.15\sqrt{k} \times 10^7$ .

It will be seen that the method described above makes possible the determination of  $k$  (or  $u$ ),  $L$ ,  $\lambda$  and  $W$  for each of the gas mixtures and the unknown gas  $X$  from observations of a single quantity  $H_0$  in pairs of gas mixtures.

## 2.6—The Halogens.

In the present section, a brief account is given of certain researches on the motion of electrons in chlorine, bromine and iodine. It is thought that such an account might prove of interest as an illustration of the method described in §2.5.

In each of the above cases it was found convenient to study mixtures of the particular halogen with other gases whose electronic properties were known.

Preliminary investigations in pure  $Cl_2$  had shown that the high chemical activity of the gas made it difficult to obtain reliable observations; thus, rapid absorption occurred, even though the electrodes were platinized, and the photo-electric current from the metal target rapidly diminished when the silver surface was exposed to the gas. These difficulties suggested the use of gas mixtures, and it was from such investigations that the method described in §2.5 arose.

(i) *Chlorine\**.—Most of the observations were made in the following mixtures:

Mixture 1. . . . . 20 per cent.  $Cl_2$  + 80 per cent.  $CO_2$ .

Mixture 2. . . . . 20 per cent.  $Cl_2$  + 80 per cent.  $He$ .

Mixture 3. . . . . 40 per cent.  $Cl_2$  + 60 per cent.  $CO_2$ .

Values of  $H_0$  were determined for each mixture and the corresponding  $(Z/p, H_0/Z)$  curve drawn. By means of equations (43) and (44) the quantities  $\sigma$  and  $\tau$  were calculated, and the three  $(\sigma, \tau)$  curves obtained; these curves for mixtures 1 and 2 are shown in figure 9. The curves  $(x, y)$  and  $(y, k)$  for the above mixtures were calculated from the known data for  $He$  and  $CO_2$ † in the manner described in the previous section (see figures 10 and 11). By

\* Bailey and Healey, *Phil.Mag.*, **19**, p. 725 (1935).

† The values of  $L$  and  $\lambda$  in  $He$  and  $CO_2$  were obtained from the results given by Townsend and Bailey (*Phil.Mag.*, **46**, p. 567, 1923) and by Skinner (*Phil.Mag.*, **44**, p. 994, 1922) and Rudd (*Phil.Mag.*, **14**, p. 1033, 1932).

means of the graphical method of solution, values of  $k$  in each mixture were determined for a number of values of  $Z/p$ . In a similar manner, the data for mixture 2 were combined with those for 3, and the data for 3 with those for 1.

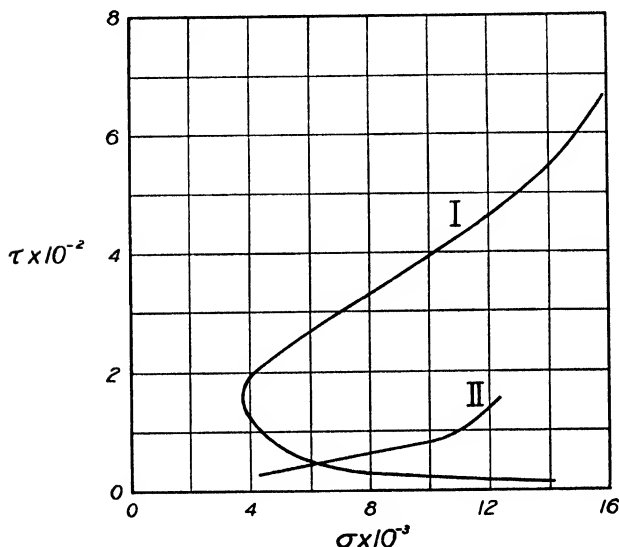
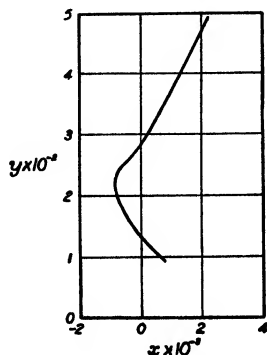


FIG. 9.

Curve I. — 20 per cent.  $Cl_2$  + 80 per cent.  $CO_2$ .  
Curve II. — 20 per cent.  $Cl_2$  + 80 per cent. He.

FIG. 10. 80 per cent.  $CO_2$  and 80 per cent. He.



In order to test the reliability of the method, a number of values of  $k$  in mixture 1 were determined by means of both the original method and a magnetic method. The various experimental data for mixture 1, and the values of  $k$  obtained by the three methods are given in table 8. This table also contains the calculated values of  $\sigma$  and  $\tau$ , together with values of  $W$  and  $\alpha/p$ .

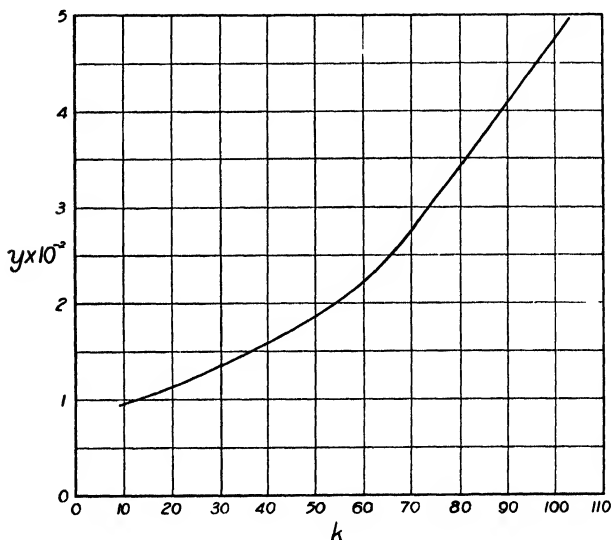


FIG. 11. 80 per cent.  $\text{CO}_2$  and 80 per cent.  $\text{He}$ .

It will be seen that the three different methods of determining  $k$  yield results which are in very satisfactory agreement. This is, perhaps, shown more clearly by figure 12, in which the values of  $k$  given in table 8 are plotted against  $Z/p$ . The chief significance of this agreement will be discussed later; however, it should be noted that these results constitute additional evidence for the reliability of the diffusion methods, as the method of mixtures—which involved the data obtained for  $\text{He}$  by means of Townsend's earlier methods, and those obtained for  $\text{CO}_2$  by means of Bailey's magnetic method—yielded values of  $k$  for mixture 1 which were in good agreement with those obtained by the original and magnetic methods.

Table 8.

Mixture 1.....20 per cent.  $Cl_2$  + 80 per cent.  $CO_2$ .

$Z$	$p$	$Z/p$	$H$	$S_3$	$S_1$	$\sigma \times 10^{-4}$	$\tau \times 10^{-2}$	$k$	$W \times 10^{-6}$	$a/p$
4	.8	5	—	.226	.316	—	—	8¶	—	.18
6	1.2	„	—	.406	.548					
2	.4	„	900	—	.450					
7.2	1.2	6	—	.396	.577	—	—	15†	—	.22
4.8	.8	„	894	—	.605					
5.6	.8	7	—	.352	.512	—	—	22¶	—	.082
8.4	1.2	„	—	.454	.606					
8.4	1.2	„	1060	—	.697					
9.6	1.2	8	802	—	.716	.42	1.11	29†	5.6	—
12	1.2	10	—	.232	.375	—	—	40¶	—	.048
8	.8	„	—	.179	.315					
8	.8	„	68.2	.231	.323					
8	.8	„	227	.454	.496	—	—	40§	—	.053
8	.8	„	497	—	.690					
12.8	.8	16	—	.180	.314	—	—	60§	—	.056
12.8	.8	„	79.4	.238	.338					
8	.5	„	520	—	.690					
8	.4	20	532	—	.690	.83	3.50	71*	12.0	—
19.2	.8	24	79.5	.213	.298	—	—	—	—	.032
9.6	.4	„	670	—	.717					
25.6	.8	32	79.5	.238	.324	—	—	84§	—	.017
25.6	.8	„	487	.499	.535					
12.8	.4	„	885	—	.754					
32	.8	40	—	.243	.284	—	—	92§	—	00
32	.8	„	431	.477	.479					
12	.3	„	787	—	.747					
12	.25	„	716	—	.747	1.80	9.32	108†	17.2	—

The values of  $H_0$  are in italics in the column under  $H$ .\*  $k$  from mixtures 1 and 2.†  $k$  from mixtures 1 and 3.¶  $k$  by original method.§  $k$  by magnetic method.‡  $k$  interpolated from fig. 12.

Values of  $L$  and  $\lambda$  for  $Cl_2$  were calculated by using equations (49) and (50); the corresponding  $(L,u)$  and  $(\lambda,u)$  curves are shown in figures 13 and 14. It will be seen that  $L$  varies very rapidly

with  $u$ , increasing by a factor of about 100 as  $u$  changes from  $3 \times 10^7$  to  $8 \times 10^7$ . The maximum in the  $\lambda$  curve at  $u = 8.1 \times 10^7$  agrees well with a maximum in the light-absorption curve at a wavelength equivalent to  $u = 8.2 \times 10^7$ .

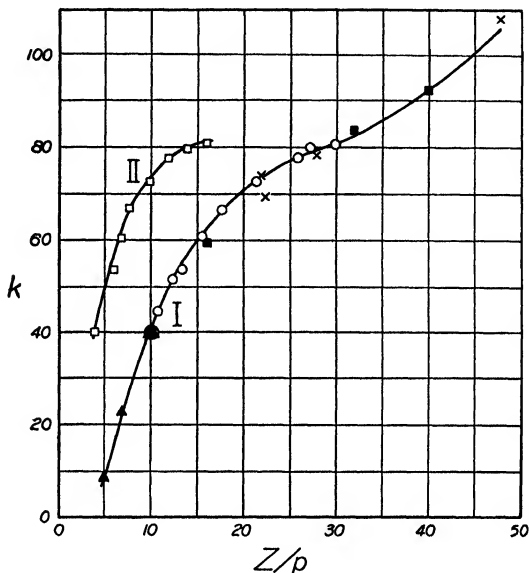


FIG. 12.

Curve I. —  $k$  for mixture 1: 20 per cent.  $Cl_2$  + 80 per cent.  $CO_2$ .  
 Curve II. —  $k$  for mixture 2: 20 per cent.  $Cl_2$  + 80 per cent.  $He$ .

Mixture 3: 40 per cent.  $Cl_2$  + 60 per cent.  $CO_2$ .

- =  $k$  from mixtures 1 and 2.
- × =  $k$  from mixtures 1 and 3.
- ▲ =  $k$  by "Original" Method.
- =  $k$  by "Magnetic" Method.
- =  $k$  from mixtures 1 and 2.

Curves showing the variation with  $Z/p$  of  $k$  and  $W$  were obtained in the manner described in the preceding section; these curves are given in figures (15) and (16).

Values of  $h$  in  $Cl_2$  were determined from measurements of  $\alpha/p$  in the mixtures by means of equation (24b) in §2.5. When the probability of attachment for the known gas is zero, this equation

takes the simplified form\*

$$h_x = 0.037 (\lambda_x + r_a L_x) k a / Z, \quad \dots\dots\dots (51)$$

where  $k$ ,  $a$  and  $Z$  refer to the particular mixture. The values of  $h$  calculated by means of equation (51) are represented by a curve in figure 17. Finally, values of  $a$  in  $Cl_2$  were calculated from these results with the aid of equation (24a) in §2.1.

(ii) *Bromine*†.—In the investigation of the motion of electrons in bromine, it was found that reliable observations of  $H_0$  could be made in the pure gas. These measurements made possible more-accurate determinations of  $\lambda$ .

Observations were made in the following mixtures:

Mixture 1.....20 per cent.  $Br_2$  + 80 per cent.  $CO_2$ .

Mixture 2.....20 per cent.  $Br_2$  + 80 per cent.  $He$ .

Mixture 3.....100 per cent.  $Br_2$ ¶.

Two sets of values of  $k$  were obtained for each mixture by combining the data for that mixture with those for each of the other two; in each case the agreement was very satisfactory.

The  $(\lambda, u)$  curve for  $Br_2$  can be derived directly from the curves  $(Z/p, H_0/Z)$  and  $(Z/p, k)$  for mixture 3. The fact that observations of  $H_0$  could be made in pure  $Br_2$  thus ensured that accurate values of  $\lambda$  were obtained; this is important, as the values of  $\lambda$  computed from observations on pairs of gas mixtures are less accurate than the corresponding values of  $L$ . However, the results obtained by the two different methods were in good agreement; for example, from the data obtained for mixtures 1 and 2, a value of  $k$  equal to 77.5 corresponds to  $Z/p = 18.5$  and  $\lambda = 1.08\%$ , while observations of  $H_0$  in pure  $Br_2$  gave  $\lambda = 1.10\%$  for  $Z/p = 18.5$ .

The methods for determining  $L$ ,  $W$ ,  $h$  and  $a$  were the same as in  $Cl_2$ . Experimental results are shown in figures 13-18.

(iii) *Iodine*‡.—Observations were made in pure  $I_2$  and in mixtures of  $I_2$  with  $He$  or  $CO_2$ :

\* This equation is derived by using the relation  $\lambda = 2.46 W^2 / u^2$  and equations (34) and (38).

† J. E. Bailey, R. E. B. Makinson and J. M. Somerville, *Phil.Mag.*, **24**, p. 177 (1937).

¶ Referred to as a mixture for the sake of convenience.

‡ Healey, *Phil.Mag.*, **26**, p. 940 (1938).

Mixture 1.....	$16\frac{2}{3}$ per cent. $I_2$ in $CO_2$ .
Mixture 2.....	$33\frac{1}{3}$ per cent. $I_2$ in $CO_2$ .
Mixture 3.....	$33\frac{1}{3}$ per cent. $I_2$ in $He$ .
Mixture 4.....	100 per cent. $I_2$ .

The graphical method makes possible three separate determinations of points on each  $(Z/p, k)$  curve by combining the results for the particular mixture with the results for each of the other three. It was found, however, that owing to the relative shapes of the  $(\sigma, \tau)$  and  $(x, y)$  curves the only reliable points on the  $(Z/p, k)$  curve for mixture 4 (pure iodine) were obtained by combining the data for this mixture with those for mixture 3. These points were supplemented by others obtained in the following manner from the  $(Z/p, k)$  curves for mixtures 1, 2 and 3:

From the definitions of  $\sigma$  and  $\tau$  in equations (43) and (44) it follows that

$$Z/p = f\sqrt{\sigma\tau}/17$$

Also,

$$x_{\mu 4} = \sigma_{\mu} - \sigma_4$$

and

$$y_{\mu 4} = \tau_{\mu} - \tau_4, (\mu = 1, 2, 3)$$

Therefore,

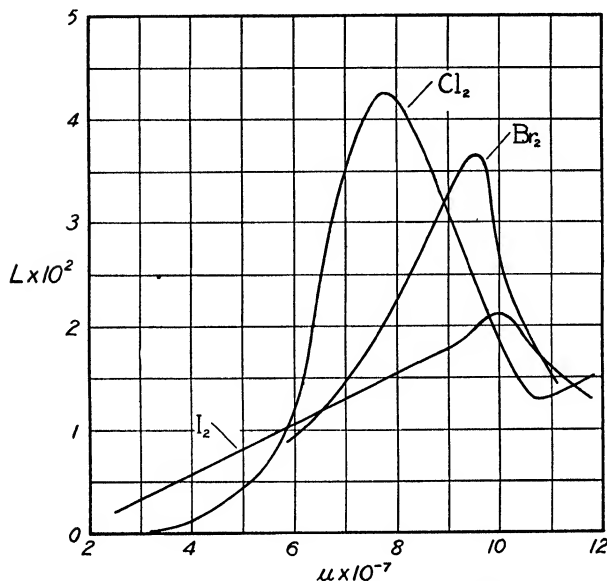
$$(Z/p)_4 = \sqrt{\sigma_4 \times \tau_4}/17 = \sqrt{(x_{\mu 4} + \sigma_{\mu})(y_{\mu 4} + \tau_{\mu})}/17.$$

Then, for a given value of  $k$ , the value of  $(Z/p)_{\mu}$  is obtained from the appropriate  $(Z/p, k)$  curve; the corresponding values of  $\sigma_{\mu}$  and  $\tau_{\mu}$  are readily determined from the experimental data, as these quantities are functions of  $(Z/p)_{\mu}$ ; also,  $x_{\mu 4}$  and  $y_{\mu 4}$  are known functions of  $k$ ; hence, the value of  $(Z/p)_4$  corresponding to a given value of  $k$  can be computed from the formula above.

The experimental results are shown in figures 13-18.

(iv) *Discussion of Experimental Results.*—The curves shown in figures 13-18 show a remarkable similarity in the properties of the three halogens.

From figure 13 it will be seen that the three  $(L, u)$  curves are of the same general shape. The variation of  $L$  with  $u$  is less pronounced in iodine than in chlorine or bromine; nevertheless, as  $u$  ranges from  $2.7 \times 10^7$  to  $10.0 \times 10^7$ ,  $L_I$  changes by a factor 7.

FIG. 13.  $(L, u)$  curves for the halogens.

The maxima of the three curves lie fairly close to one another, the value of  $L_{max}$ , diminishing as the molecular weight increases, as is shown in the following table.

Table 9.

Halogen	Value of $L_{max}$ .	Maximum occurs at $u =$
$Cl_2(71)$	$4.25 \times 10^{-2}$	$7.8 \times 10^7$
$Br_2(160)$	$3.65 \times 10^{-2}$	$9.6 \times 10^7$
$I_2(254)$	$2.1 \times 10^{-2}$	$10.0 \times 10^7$

Figure 14 shows that the three  $(\lambda, u)$  curves are also of the same general form. As  $u$  increases,  $\lambda$  rises from small values to a maximum, falls slightly, and then rises again. Here, as in

figure 13, the variations in the iodine curve are not so marked as those corresponding to chlorine and bromine.

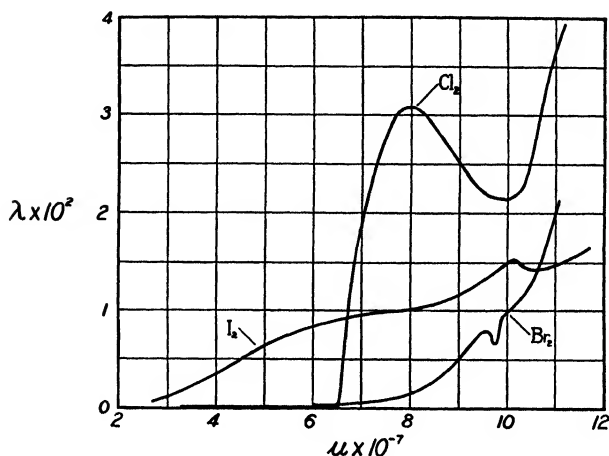


FIG. 14.  $(\lambda, u)$  curves for the halogens.

The positions and values of the maxima are given in table 10.

Table 10.

Halogen	Value of $\lambda_{max.}$	Maximum occurs at $u =$
$Cl_2$	$3.08 \times 10^{-2}$	$8.1 \times 10^7$
$Br_2$	$0.78 \times 10^{-2}$	$9.6 \times 10^7$
$I_2$	$1.52 \times 10^{-2}$	$10.1 \times 10^7$

For each halogen there is a rough agreement between a maximum in the light-absorption curve and the maximum in the  $(\lambda, u)$  curve (see table 11).

There is a further interesting correlation between the light-absorption and the  $(\lambda, u)$  curves; from the colours of the halogens it is evident that, as the wavelength diminishes from the infra-red, absorption would become appreciable first in iodine, then in chlorine

and finally in bromine; and from figure 14 it will be seen that, as  $u$  increases from small values,  $\lambda$  becomes appreciable in these gases in the same order.

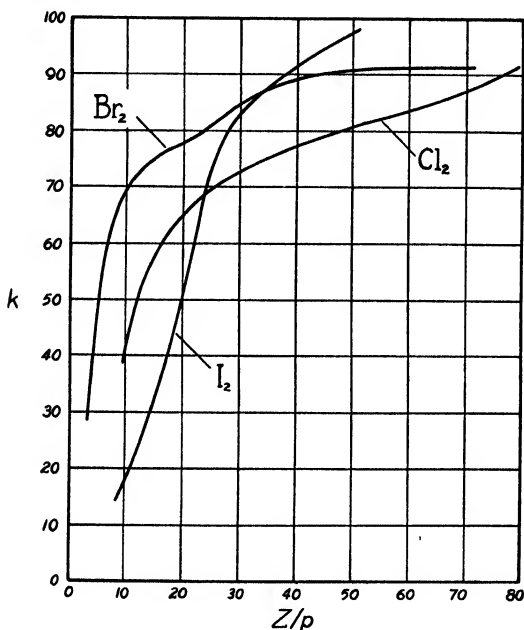


FIG. 15. ( $Z/p, k$ ) curves for the halogens.

Table 11.

Halogen	$\lambda_{max.}$ occurs at $u =$	Maximum in Light-Absorption occurs at $u =$
$Cl_2$	$8.1 \times 10^7$	$8.2 \times 10^7$
$Br_2$	$9.6 \times 10^7$	$10.3 \times 10^7$
$I_2$	$10.1 \times 10^7^*$	$9.4 \times 10^7$

\* This value of  $u$  is also in fair agreement with the value of the excitation-potential 2.3 volts given by Mohler and Foote (*Handbuch d. Phys.*, 23, p. 762).



The similarity in the properties of the three halogens is further illustrated by the  $(h, u)$  curves given in figure 17. It should be noted that larger values of  $h$  occur in iodine than in bromine or chlorine; these values are the largest yet recorded for any gas. For iodine, the large values of  $h$  in the range of velocities from  $7 \times 10^7$  to  $10 \times 10^7$  must tend to mask the correlation between the light-absorption and  $(\lambda, u)$  curves.

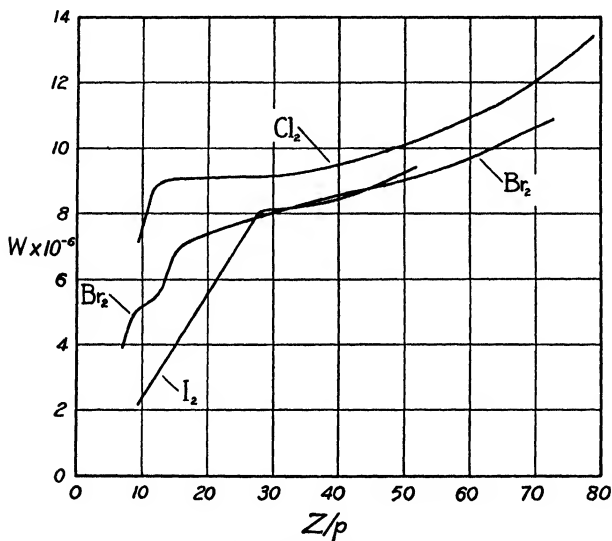


FIG. 16.  $(Z/p, W)$  curves for the halogens.

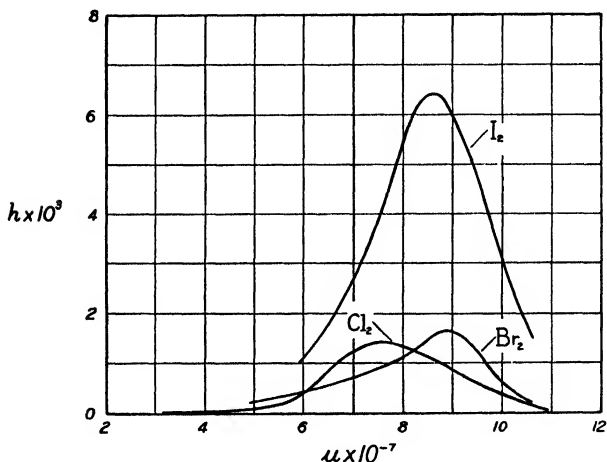
It is interesting to enquire whether the ions initially formed by attachment in these halogens are of molecular or atomic mass; the latter value of the mass seems the more probable, as in each case  $h$  is small at low electron energies ( $< \frac{1}{2}$  volt), but rises to large values at energies which do not differ greatly from the energy of dissociation of the molecule (see table 12).

The fact that both  $\lambda$  and  $h$  are small for  $u < 3 \times 10^7$  shows that, in spite of the large electron-affinities of the halogens, the behaviour of electrons in these gases is similar to that in the inert gases over a considerable range of velocities.

It will be seen from figure 18 that the values of  $a/p$  in iodine are of the order 10 times greater than the corresponding values

Table 12.

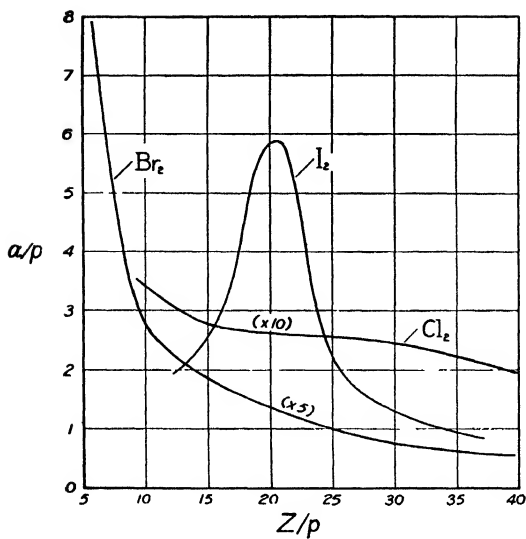
Halogen	$h_{max.}$ occurs at $u =$	Energy of Dissociation* is equivalent to $u =$
$Cl_2$	$7.6 \times 10^7$	$9.3 \times 10^7$
$Br_2$	$9.9 \times 10^7$	$8.4 \times 10^7$
$I_2$	$8.6 \times 10^7$	$7.2 \times 10^7$

FIG. 17. ( $h, u$ ) curves for the halogens.

for chlorine and bromine. The curve rises to a maximum at  $Z/p = 20$ , then falls away; turning-points in the two other ( $Z/p, a/p$ ) curves possibly occur in the range  $Z/p < 5$ .

In figure 15 the ( $Z/p, k$ ) curves are given, that for iodine being similar in shape to the other two. This similarity is more marked

\* Franck and Jordan, *Handbuch d. Phys.*, 23, p. 761. In this reference, the respective energies given for  $Cl_2$ ,  $Br_2$  and  $I_2$  are  $57 \times 10^3$ ,  $46 \times 10^3$  and  $34.5 \times 10^3$  calories per gramme molecule. The International Critical Tables (Vol. 5) give the values 2.835 volts ( $u = 9.5 \times 10^7$ ), 1.961 volts ( $u = 8.3 \times 10^7$ ) and 1.532 volts ( $u = 7.4 \times 10^7$ ). N. E. Bradbury (*Journ. Chem. Phys.*, 2, p. 833, 1934) states that the energy of dissociation of  $Cl_2$  is about 1.5 volts ( $u = 7.3 \times 10^7$ ).

FIG. 18  $(Z/p, a/p)$  curves for the halogens

in the  $(Z/p, W)$  curves shown in figure 16; in this case each curve rises steeply at first, then bends sharply, whereafter the gradient is considerably reduced.



### III

## THE VELOCITY - DISTRIBUTION OF SLOW ELECTRONS IN GASES

### 3.1—The Drift Velocity and the Coefficient of Diffusion.

In chapters 1 and 2, a number of formulae were used which contain numerical factors depending upon the velocity-distribution of the electrons. In the present chapter it is proposed to show how these factors are related to the velocity-distribution, to indicate how the various experiments allow some estimate to be made of the distribution and finally to make estimates of the accuracy of the formulae mentioned above.

We begin by discussing the mean free path  $l$ . Consider a large number of electrons making collisions in the neighbourhood of a point  $P$  in the gas ; and let  $N_0$  be the number having velocities between  $U$  and  $U + dU$ ,  $\beta$  be the probability that one of these electrons will make a collision in moving unit distance in the radial direction, and  $l_v$  be the associated mean free path. It can then be simply shown\* that the number  $N$  of these  $N_0$  which arrive at a radial distance  $r$  from  $P$  (the distribution is spherically symmetric, as all directions of motion after a collision are equally probable) is given by the relation

$$N = N_0 e^{-\beta r} ;$$

so that

$$\begin{aligned} l_v &= \frac{1}{N_0} \int_0^{\infty} N_0 e^{-\beta r} \beta r . dr \\ &= \frac{1}{\beta} . \end{aligned}$$

The mean of the squares of the individual paths,

$$\frac{1}{N_0} \int_0^{\infty} N_0 e^{-\beta r} \beta r^2 . dr ,$$

therefore equals  $2l_v^2$ .

\* Townsend, "Electricity in Gases," p. 82.

In the above discussion it has been assumed for the sake of simplicity that there is no applied field; it is clear, however, that for a given value of  $U$  the quantity  $l_U$  is not appreciably affected by the presence of a field. Further, it is usually assumed in this work that  $l_U$  does not vary greatly with  $U$ ; this assumption is supported by the experimental results for the majority of gases, and by the fact that most indications point to a fairly narrow distribution of velocities.

In §1.1 it was shown that in the absence of a field the coefficient of diffusion  $K$  is given by equations of the form

$$nV_z = -K \frac{\partial n}{\partial z}.$$

This coefficient can also be expressed in terms of the rate of change of the mean square of the distances of the electrons from any point, and in terms of the mean free path and the average velocity of agitation\*. These expressions are obtained in the following manner.

For simplicity, let the distribution be symmetrical about the centre  $O$ †; the electron density  $n$  is then a function of the radial distance  $r$ . The number of electrons included between spheres of radii  $r$  and  $r + dr$  is  $4\pi r^2 n \cdot dr$ , and the mean square of their distances from  $O$  is

$$R^2 = \frac{\int_0^{r'} 4\pi n r^4 \cdot dr}{\int_0^{r'} 4\pi n r^2 \cdot dr}.$$

In these integrals the upper limit  $r'$  is taken very large, so that  $n = 0$  and  $dn/dr = 0$  when  $r = r'$ . The total number of particles is constant; hence, when differentiated with regard to time, the above equation becomes

$$\int_0^{r'} r^4 \frac{dn}{dt} \cdot dr = \frac{d(R^2)}{dt} \cdot \int_0^{r'} n r^2 dr.$$

\* "Electricity in Gases," pp. 85-88.

† This investigation also holds generally, for as far as the radial motion from  $O$  is concerned, it is immaterial whether the distribution between two concentric spheres of radii  $r$  and  $r + dr$  is uniform or not.

The rate of increase of the number of particles in the included space is equal to the difference between the rates at which electrons flow across the two surfaces. Thus, representing the radial velocity of transport by  $V_r$ ,

$$4\pi r^2 \frac{dn}{dt} dr = 4\pi r^2 (n V_r) - \left[ 4\pi r^2 (n V_r) + \frac{d}{dr} (4\pi r^2 \cdot n V_r) \cdot dr \right],$$

or

$$r^2 \frac{dn}{dt} = -\frac{d}{dr} (r^2 \cdot n V_r) = \frac{d}{dr} \left( r^2 K \frac{dn}{dr} \right).$$

Hence,

$$\int_0^{r'} r^2 \frac{d}{dr} \left( r^2 K \frac{dn}{dr} \right) dr = \frac{d(R^2)}{dt} \int_0^{r'} nr^2 \cdot dr.$$

Integrating by parts, and making use of the conditions  $n = 0$  and  $dn/dr = 0$  at  $r = r'$ , it is simply shown that the left-hand side is equal to

$$- 2K \int_0^{r'} r^3 \frac{dn}{dr} dr = 6K \int_0^{r'} nr^2 \cdot dr,$$

so that

$$6K = d(R^2)/dt. \dots\dots\dots (52)$$

Hence the rate of change of the mean square of the distances of any distribution from a point is  $6K$ .

The expression for  $K$  in terms of  $l$  and  $\bar{U}$  follows from equation (52) when it is remembered that all directions of motion after a collision are equally probable, and that in all the cases considered the agitational velocity does not vary appreciably between collisions.

Let  $P$  (see figure 19) be a point on the surface of a sphere of radius  $r$  and centre  $O$ , and let  $Q$  be a point on the surface of a small sphere of radius  $x$  and centre  $P$ ; then the mean square of the distances of the points on the surface of the small sphere from  $O$  is

$$\frac{1}{4\pi x^2} \int_0^\pi (r^2 + x^2 + 2rx \cos \theta) 2\pi x^2 \sin \theta \cdot d\theta = r^2 + x^2,$$

where  $\theta$  is the angle which  $QP$  makes with  $OP$ . The mean square

of the distances from  $O$  is therefore increased by  $x^2$  when the electrons in the neighbourhood of the surface of the large sphere traverse free paths of length  $x$ . If, for the moment, we consider only those electrons having velocities between  $U$  and  $U + dU$ , it is clear that when several consecutive paths are traversed the change in the mean

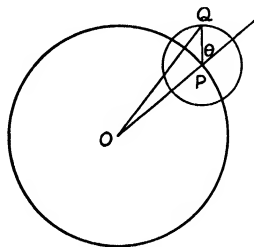


FIG. 19.

square of the distances will be  $\Sigma x^2$  in the time  $\Sigma x/U$ ; hence the rate of change of the mean square is  $U(\Sigma x^2/\Sigma x) = 2l_U U$ , which is independent of  $r$ . The coefficient  $K$  for the entire group is therefore given by the equation

$$K = \frac{1}{3} \overline{(l_U U)},$$

the bar over the expression on the right-hand side denoting an average value. As it is customary to assume that  $l_U$  does not vary rapidly with  $U$ , this equation is usually written

$$K = \frac{1}{3} \overline{l_U}. \quad \dots\dots\dots (53)$$

Equation (53) can also be obtained more directly by considering the number of electrons flowing per second across a small area which is normal to the density gradient\*. Let this area  $dS$  be at the origin of coordinates in the plane  $z = 0$ , and let the density  $n$  at any point in the neighbourhood of the origin be given by

$$n = n_0 + z \frac{dn}{dz}.$$

\* See Huxley, *Phil.Mag.*, 23, pp. 211-217 (1937); and Townsend, *Phil.Mag.*, 23, p. 485 (1937).



For simplicity, assume that all the electrons have the same velocity  $U$ . Then, using spherical co-ordinates, the number of electrons per second which make a collision within the volume element  $d\tau$  at  $(r, \theta, \Phi)$  is

$$n.d\tau.(U/l_v) = n(U/l_v) r^2 \sin \theta . d\Phi . d\theta . dr,$$

and of these, a proportion  $e^{-r/l_v} dS \cdot \cos \theta / 4\pi r^2$  cross  $dS$  without making a further collision. Hence the flow of electrons  $\eta_1$  per second across  $dS$  from points in the space  $z > 0$  is equal to

$$\begin{aligned} \frac{U}{l_v} \cdot \frac{dS}{4\pi} \int_0^\infty \int_0^{\pi/2} \int_0^{2\pi} \left( n_0 + r \cos \theta \frac{dn}{dz} \right) e^{-r/l_v} \cdot \sin \theta \cos \theta d\Phi . d\theta . dr \\ = \frac{dS}{2} \left[ \frac{n_0 U}{2} + \frac{1}{3} l_v U \left( \frac{dn}{dz} \right) \right]. \end{aligned}$$

The use of the above expression for  $n$  in this integral is justified, as it is clear that in all the cases considered, essentially all of the electrons crossing  $dS$  make a collision in the immediate neighbourhood of the origin before doing so. The rate of flow of electrons across  $dS$  from points on the other side of the plane  $z = 0$  is similarly given by

$$\eta_2 = \frac{dS}{2} \left[ \frac{n_0 U}{2} - \frac{1}{3} l_v U \left( \frac{dn}{dz} \right) \right],$$

so that the total rate of flow in the positive direction of  $z$  is

$$\eta_2 - \eta_1 = - \frac{1}{3} l_v U \left( \frac{dn}{dz} \right) . dS.$$

For electrons having a distribution of velocities, this equation becomes

$$\eta_2 - \eta_1 = - \frac{1}{3} \overline{(l_v U)} \frac{dn}{dz} . dS,$$

so that, as  $\eta_2 - \eta_1 = - K \frac{dn}{dz} . dS$ , we have

$$K = \frac{1}{3} \overline{(l_v U)},$$

as before.

The formulae for  $W$  given in §1.6 for the case in which all the electrons have the same velocity of agitation  $U$  are not quite correct, as it was there assumed that, in the mean time  $l_U/U$  between collisions, the displacement in a direction parallel to the field was  $\frac{1}{2}(Ze/m)(l_U/U)^2$ . The correct formula can be derived in the following manner\*.

Consider an electron making a collision at  $O$ ; let the ensuing free path  $OP$ , in the absence of the field be of length  $x$ , making an angle  $\theta$  with the  $z$ -axis (see figure 20). When  $Z$  is applied (it is assumed that  $Z$  is not too large) this path is altered to the curved path  $OQ$ . The time of transit is  $x/U$  and the acceleration normal

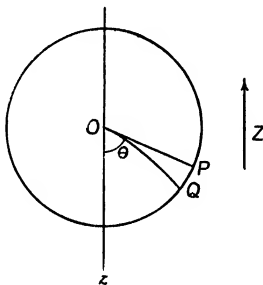


FIG. 20.

to  $OP$  is  $(Ze/m) \sin \theta$ , so that the displacement  $PQ$  is  $\frac{1}{2}(Ze/m) \sin \theta.(x/U)^2$ ; hence the displacement parallel to  $z$  is

$$\frac{1}{2}(Ze/m) \sin^2 \theta.(x/U)^2.$$

As all directions of motion after a collision are equally probable, the mean displacement for a large number of electrons having the free path  $x$  is

$$\begin{aligned} & \frac{1}{2}(Ze/m) \cdot (x/U)^2 \int_0^\pi \frac{\sin^3 \theta}{2} d\theta \\ &= \frac{1}{3}(Ze/m) \cdot (x/U)^2. \end{aligned}$$

\* Townsend, *Phil.Mag.*, 22, pp. 151-153 (1936).

Then, averaging for all the free paths, we obtain the following equation giving the mean displacement  $\Delta z$ :

$$\Delta z = \frac{2}{3}(Ze/m) \cdot (l_U/U)^2.$$

Over a large number of free paths  $N$ , the mean displacement of a single electron due to the field  $Z$  is  $N \cdot \Delta z$  in time  $Nl_U/U$ , so that the drift velocity  $W_U$  of electrons having the same velocity of agitation  $U$  is given by

$$W_U = \frac{2}{3} \cdot \frac{Ze}{m} \left( \frac{l_U}{U} \right).$$

For the general case we then have

$$W = \frac{2}{3} \cdot \frac{Ze}{m} \left( \overline{\frac{l_U}{U}} \right);$$

or, making the usual assumption that  $l_U$  does not vary sharply with  $U$ ,

$$W = \frac{2}{3} \cdot \frac{Zel}{m} \left( \overline{\frac{1}{U}} \right). \dots\dots\dots (54)$$

Huxley\* obtains the equation giving the transport of electrons in the direction of the field by a method similar to that used earlier in this section to obtain the coefficient of diffusion.

Let  $Z$  be counter to the direction of the  $z$ -axis. Then consider the number of electrons flowing per second across a small

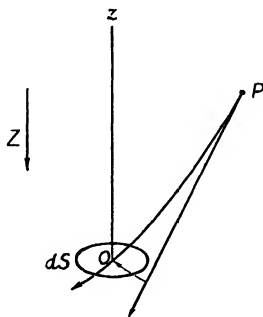


FIG. 21.

\* *Phil. Mag.*, 23, pp. 211-217 (1937).

area  $dS$ , from points  $P$  in the space  $z > 0$  (see figure 21); as before, it is assumed that  $n = n_0 + z \frac{dn}{dz}$  in the neighbourhood of  $O$ .

When  $Z$  is not too large, the curvature of the paths is slight, so that the length of the path from  $P$  to  $O$  is very nearly equal to the direct distance  $r$ ; the principal effect of the field is, then, to change the angle of incidence from  $\theta$  to  $\theta + \alpha$ .

The velocity parallel to  $Oz$  acquired during the path  $PO$  is  $(Ze/m).(r/U)$ , so that, from a triangle of velocities it is clear that

$$\sin \alpha = \frac{Zer}{mU^2} \sin \theta.$$

Using the same notation as before, it is then seen that the number of electrons per second which collide within a small volume element  $d\tau$  at  $P$  and then traverse  $dS$  without further collision is

$$\frac{nU}{l_U} e^{-r/l_U} \frac{dS \cdot \cos(\theta + \alpha)}{4\pi r^2} d\tau.$$

As  $Z$  is not too large,  $\cos \alpha$  may be put equal to unity in the expansion of  $\cos(\theta + \alpha)$ . The flux  $\eta_1$  is then given by

$$\begin{aligned} \eta_1 &= \frac{U}{l_U} \cdot \frac{dS}{4\pi} \int_0^\infty \int_0^{\pi/2} \int_0^{2\pi} \left( n_0 + r \cos \theta \cdot \frac{dn}{dz} \right) e^{-r/l_U} \sin \theta \cdot \\ &\quad \left( \cos \theta - \frac{Zer}{mU^2} \sin^2 \theta \right) \cdot d\phi d\theta \cdot dr \\ &= \frac{dS}{2} \left[ \frac{n_0 U}{2} + K_U \left( 1 - \frac{9}{4} \cdot \frac{W_U}{U} \right) \frac{dn}{dz} - n_0 W_U \right], \end{aligned}$$

where  $K_U = \frac{1}{3} (l_U U)$  and  $W_U = \frac{2}{3} \frac{Ze}{m} \left( \frac{l_U}{U} \right)$ . The number of electrons crossing  $dS$  per second in the reverse direction is similarly given by

$$\eta_2 = \frac{dS}{2} \left[ \frac{n_0 U}{2} - K_U \left( 1 - \frac{9}{4} \frac{W_U}{U} \right) \frac{dn}{dz} + n_0 W_U \right],$$

so that the net transport in the direction of the  $z$ -axis is

$$\eta_2 - \eta_1 = \left[ -K_U \left( 1 - \frac{9}{4} \frac{W_U}{U} \right) \frac{dn}{dz} + n_0 W_U \right] dS.$$

In all the experiments considered, the drift velocity is at most a few per cent. of the agitational velocity, so that the term  $W_U/U$  may be omitted from the above expression.

Considering the entire group of electrons, having velocities distributed about a mean value  $\bar{U}$ , the equation giving the transport of electrons in a direction counter to the field is then obtained:

$$nV_z = -K \frac{\partial n}{\partial z} + nW,$$

where  $K = \frac{1}{3} \overline{l_U U}$  and  $W = \frac{2}{3} \frac{Ze}{m} \overline{\left( \frac{l_U}{U} \right)}$ .

### 3.2—The Energy Factor.

In obtaining the relation

$$\frac{PV_z}{K} = -\frac{\partial P}{\partial z} + neZ$$

in §1.3 it was assumed that in a steady state the expression  $PV_z/K$ , which is given by the third of equations (10a), represents the momentum lost by the electrons per second per unit volume in collisions with molecules. This identification is, in general, not quite accurate, so that the relation

$$\frac{W}{K} = \frac{neZ}{P} = \frac{3Ze}{mu^2} = \frac{NeZ}{kII}$$

can not always be regarded as exact\*. It will then be seen that the values obtained for  $k$  (and  $u$ ) may be somewhat in error.

Using the results obtained in the previous section, it is easily shown that

$$\frac{W}{K} = 2 \left( \frac{b}{a} \right) \frac{Ze}{mu^2},$$

\* Townsend, *Phil.Mag.*, 23, p. 481 (1937).

where  $au = \bar{U}$  and  $b/u = \overline{(1/U)}$ . In general,  $a < 1$  and  $b > 1$ , equation (11a) and the resulting expressions for  $W/K$  being exact only when  $b/a = 3/2$ , as in the Maxwellian distribution, where

$$a = \sqrt{8/3\pi} = 0.92, \text{ and } b = \frac{3}{2}\sqrt{8/3\pi} = 1.38.$$

From the above discussion it will be seen that  $W/K$  may be expressed by the relation

$$\frac{W}{K} = \frac{NeZ}{k_1 H},$$

where  $k_1 = \frac{3}{2}(a/b)k$ .

For a Maxwellian distribution,  $k_1 = k$ ; and for the case in which all the velocities are equal,  $k_1 = 1.5k$ .

### 3.3—The Mean Energy lost at a Collision.

A more rigorous derivation of the quantity  $\lambda$  than that given in §1.7 is the following.

Consider the  $dN$  electrons having velocities between  $U$  and  $U + dU$ . Then, in moving a distance  $\delta$  in the direction of drift each of these particles makes  $(U/l) \cdot (\delta/W_U)$  collisions with gas molecules, so that we have

$$(\lambda_U \cdot \frac{1}{2} mu^2) \frac{U}{l} \cdot \frac{\delta}{W_U} = Ze\delta,$$

that is,

$$\lambda_U = 3 \frac{W_U^2}{U^2}.$$

Then, in the time  $t$ , the number of collisions made by the entire group of  $N$  electrons is

$$\int_{-\frac{U}{l}}^U t \cdot dN = Nt\bar{U}/l;$$

and the total energy lost by the electrons in these collisions is

given by

$$\begin{aligned} & \int \lambda_{U^{-1}} \frac{1}{2} m u^2 \cdot \frac{U}{l} t \cdot dN \\ &= \frac{3}{2} m W^2 \frac{t}{l} \left[ \overline{(U^{-1})} \right]^{-2} \int U^{-1} dN \\ &= \frac{3}{2} N m W^2 \frac{t}{l} \left[ \overline{(U^{-1})} \right]^{-1}; \end{aligned}$$

so that

$$\lambda = 3 W^2 u^{-2} / \left( \overline{U \cdot (U^{-1})} \right) . *$$

For the case in which all the electrons have the same velocity,

$$\lambda = 3 \frac{W^2}{u^2} = 4.5 \frac{W^2}{u_1^2},$$

where

$$u_1 = 1.15 \sqrt{k_1} \times 10^7.$$

For a Maxwellian distribution, the proportion of electrons having velocities between  $U$  and  $U + dU$  is given by an expression of the form

$$\frac{dN}{N} = A \cdot e^{-B U^2} \cdot U^2 \cdot dU,$$

so that

$$\overline{U} \cdot \overline{(U^{-1})} = \frac{4}{\pi}.$$

In this case, therefore,

$$\lambda = 2.356 \frac{W^2}{u^2} = 2.356 \frac{W^2}{u_1^2}.$$

### 3.4—Formulae Used in the Determination of the Drift Velocity.

In Townsend's method of obtaining  $W$  by measuring the deflection  $\theta$  of the stream when a magnetic field  $H$  is applied parallel

\* This formula was given by Dr. L. G. H. Huxley in a private communication to Prof. V. A. Bailey.

to the slit (that is, parallel to the  $y$ -axis) the formula used is (see §1.5)

$$\frac{HW}{Z} = \tan \theta.$$

Huxley\* has shown that this formula is not exact, and obtains the result

$$\tan \theta = \frac{W_x}{W_z},$$

where

$$W_x = \frac{Z}{H} \left[ \frac{\omega^2 T^2}{1 + \omega^2 T^2} \left( \frac{1}{3} + \omega^2 T^2 \right) \right],$$

$$W_z = \frac{2}{3} \cdot \frac{Z}{H} \left[ \frac{\omega T}{1 + \omega^2 T^2} \left( 1 + \frac{\omega^2 T^2}{1 + \omega^2 T^2} \right) \right],$$

and

$$T = \frac{l}{U}, \quad \omega = \frac{He}{m}.$$

A formula given by Townsend† is a special case of the above result, corresponding to  $\omega T \ll 1$ ; this relation is

$$\tan \theta = \frac{1}{2} \omega (\overline{T^2}) / \overline{T}.$$

The values of  $H$  used in these experiments were such that the above condition is fulfilled; so that we have

$$\begin{aligned} \tan \theta &= \frac{1}{2} \frac{Hel}{m} \left( \overline{\frac{1}{U^2}} \right) / \left( \overline{\frac{1}{U}} \right) \\ &= \frac{3}{4} \frac{HW}{Z} \left( \overline{\frac{1}{U^2}} \right) / \left[ \left( \overline{\frac{1}{U}} \right) \right]^2, \end{aligned}$$

or

$$W = \frac{4}{3} \cdot \frac{Z}{H} \cdot \tan \theta \left[ \left( \overline{\frac{1}{U}} \right) \right]^2 / \left( \overline{\frac{1}{U^2}} \right).$$

\* *Phil.Mag.*, **23**, pp. 219-229 (1937).

† *Phil.Mag.*, **23**, p. 880 (1937).



For the case in which all the electrons have the same velocity, we then have

$$W = 1.33 \frac{Z}{H} \tan \theta.$$

For a Maxwellian distribution of velocities, this formula becomes

$$\begin{aligned} W &= \frac{8}{3\pi} \cdot \frac{Z}{H} \cdot \tan \theta \\ &= 0.85 \frac{Z}{H} \tan \theta. \end{aligned}$$

In Bailey's method of determining  $W$  (see §2.4), the magnetic field  $H$  is applied parallel to the electric field  $Z$ . Under these circumstances, it can be shown\* that

$$K_x = K_y = \frac{1}{3} \left( \frac{lU}{1 + \omega^2 T^2} \right),$$

$K_z$  still having the value  $\frac{1}{3} (\overline{lU})$ .

When  $H = H_0$ ,  $\Phi_0 = k_1$ . Thus, when all the electrons have the same velocity

$$k_1 = \Phi_0 = \frac{K_z}{K_x} = 1 + \omega_0^2 T^2,$$

that is,

$$\frac{H_0 e}{m} \cdot \frac{l}{U} = \sqrt{k_1 - 1}$$

or

$$W = 0.67 \frac{Z}{H_0} \sqrt{k_1 - 1}.$$

The corresponding result for the general case is simplified by the fact that the values of  $H_0$  are such that  $\omega_0^2 T^2 \gg 1$ , so that  $\omega_0^2 T^2$  may be put equal to  $\omega_0^2 T^2 + 1$ . Using this approximation,

\* Huxley, *Phil. Mag.*, 23, p. 217 (1937).

it is simply shown that

$$\begin{aligned} k_1 &= \Phi_0 = \frac{K_z}{K_x} \\ &= \omega_0^2 \bar{U} / (\bar{U}^3) \\ &= \left\{ \frac{3}{2} \frac{H_0 W}{Z} / (\bar{U}^{-1}) \right\}^2 \bar{U} / (\bar{U}^3), \end{aligned}$$

or

$$\begin{aligned} W &= \frac{2}{3} \frac{Z}{H_0} \sqrt{k_1} \left\{ (\bar{U}^3) \left[ (\bar{U}^{-1}) \right]^2 / \bar{U} \right\}^{\frac{1}{2}} \\ &= \frac{2}{3} \frac{Z}{H_0} \sqrt{k_1} \left\{ (\bar{U}^{-1}) \cdot (\bar{U}^3) / \bar{U}^2 \right\}^{\frac{1}{2}}. \end{aligned}$$

For a Maxwellian distribution we then have

$$W = 1.07 \frac{Z}{H_0} \sqrt{k_1}.$$

A more exact formula for this case is

$$W = 1.07 \frac{Z}{H_0} \sqrt{k_1 - \frac{3}{2k_1}},$$

obtained by expanding  $\left(1 + \frac{1}{\omega_0^2 T^2}\right)^{-1}$  and neglecting powers

of  $1/\omega_0^2 T^2$  higher than the first. This result shows that the error introduced by setting  $\omega_0^2 T^2$  equal to  $\omega_0^2 T^2 + 1$  is only about one per cent for values of  $k_1$  as low as 10.

### 3.5—The Probable Distribution.

It will be seen from the preceding sections that the formulae used in Chapters 1 and 2 to calculate  $k$ ,  $u$ ,  $W$ ,  $L$ ,  $\lambda$  and  $h$  may be appreciably in error\*.

Thus, in §3.2 it has been shown that the values  $k_1$  given for  $k$  by both methods are related to the true values in the following

\* J. W. Reed, *Amalg Wireless Assoc Tech. Rev*, 5, p. 21 (1940)

manner :

$$k_1 = \frac{3}{2} k \left\{ \bar{U} \cdot u^{-2} / (\bar{U}^{-1}) \right\}.$$

The other correct formulae, for Townsend's method and Bailey's method, are given in the following table.

Table 13.

Townsend's Method	$W = \frac{4}{3} \frac{Z}{H} \tan \theta \left[ (\bar{U}^{-1}) \right]^2 / (\bar{U}^{-2}).$ $L = \frac{3}{2} W \left( \frac{pm}{Ze} \right) / (\bar{U}^{-1}).$ $\lambda = 3W u^{-2} \left\{ (\bar{U}^{-1}) \cdot \bar{U} \right\}^{-1}.$
Bailey's Method	$W = \sqrt{\frac{2}{3}} \frac{Z}{H_0} k^{\frac{1}{2}} \left\{ (\bar{U}^{-1})(\bar{U}^3) u^{-2} \right\}^{\frac{1}{2}}.$ $L = \frac{3}{2} W \left( \frac{pm}{Ze} \right) / (\bar{U}^{-1}).$ $\lambda = 3W u^{-2} \left\{ (\bar{U}^{-1}) \cdot \bar{U} \right\}^{-1}.$ $h = \frac{\alpha LW}{p} (\bar{U})^{-1}.$

The formulae actually used by Townsend and Bailey are given below, the subscripts *T* and *B* being used to denote the values obtained for the various quantities.

Table 14.

Townsend's Method	$u_T = 1.15 k_1^{\frac{1}{2}} \times 10^7.$ $W_T = \frac{Z}{H} \tan \theta.$ $L_T = \frac{1}{0.815} W_T \left( \frac{pm}{Ze} \right) u_T.$ $\lambda_T = 2.46 W_T^2 u_T^{-2}.$
Bailey's Method	$u_B = 1.15 k_1^{\frac{1}{2}} \times 10^7.$ $W_B = \frac{Z}{H_0} (k_1 - 1)^{\frac{1}{2}}.$ $L_B = \frac{1}{0.815} W_B \left( \frac{pm}{Ze} \right) u_B.$ $\lambda_B = 2.46 W_B^2 u_B^{-2}.$ $h_B = \frac{\alpha L_B W_B}{p} u_B^{-1}.$

The relations set out above can be used to derive the following table giving the ratios of the values obtained by Townsend and Bailey to the true values of the various quantities. Four velocity-distributions are dealt with; these are:

- I All the electrons have the same velocity of agitation,
- II  $dN/N = A. \exp(-BU^4) \cdot U^4 \cdot dU$ ;
- III  $dN/N = A. \exp(-BU^4) \cdot U^2 \cdot dU$ ;
- IV  $dN/N = A. \exp(-BU^2) \cdot U^2 \cdot dU$  (Maxwellian).

Table 15.

Ratio	I	II	III	IV
$k_T/k$	1.5	1.31	1.14	1
$u_T/u$	1.22	1.14	1.07	1
$W_T/W$	0.75	0.83	1.06	1.18
$L_T/L$	0.75	0.86	1.16	1.33
$\lambda_T/\lambda$	0.31	0.47	0.97	1.45
$k_B/k$	1.5	1.31	1.14	1
$u_B/u$	1.22	1.14	1.07	1
$W_B/W$	1.5	1.22-1.28*	1.04-1.10*	0.90-0.94*
$L_B/L$	1.5	1.30	1.18	1.05
$\lambda_B/\lambda$	1.23	1.07	0.99	0.90
$\alpha_B/\alpha$	1	1	1	1
$h_B/h$	1.84	1.39	1.13	1.06
* The lower value corresponds to $k_1 = 10$ , the higher to $k_1 \geq 100$ For the ratios $L_B/L$ , $\lambda_B/\lambda$ and $h_B/h$ , the respective values 1.26, 1.08 and 0.93 have been chosen, corresponding to $k_1 = 30$ .				

The variation of a number of these ratios with the velocity-distribution is shown schematically in figure 22.

In figure 23 are shown the distribution curves (for the same most-probable velocity) corresponding to II, III and IV.

In all cases so far investigated by both methods there is a remarkably close agreement between corresponding sets of results, so that the prevailing distribution must be such that  $W_T/W$  is very nearly equal to  $W_B/W$ .

This condition is fulfilled by the distribution III :

$$dN/N = A. \exp (-BU^4).U^2.dU. \dots\dots\dots(55)$$

The bulk of evidence suggests that the distribution curve is of the same form as the curves shown in figure 23. A study of the formulae for  $W$  in table 13 and the very close agreement between the corresponding ratios for the distribution III then shows that the actual distribution is not likely to be very different from that given by (55). This conclusion is supported by an

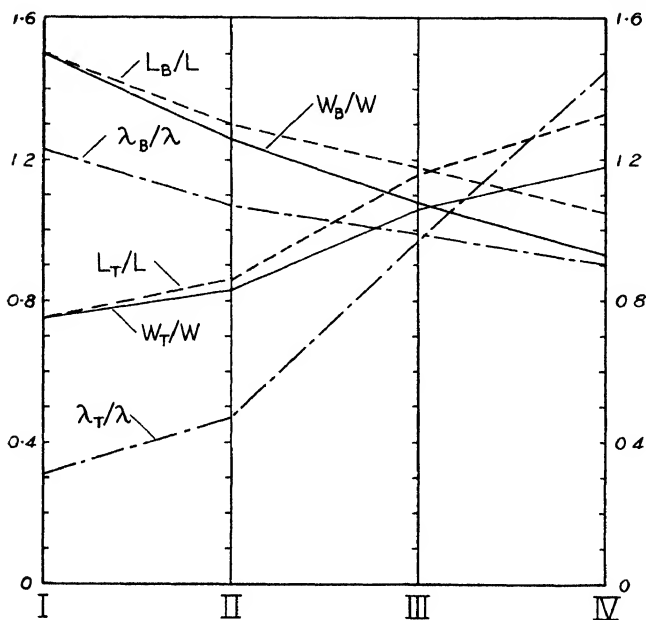


FIG. 22.

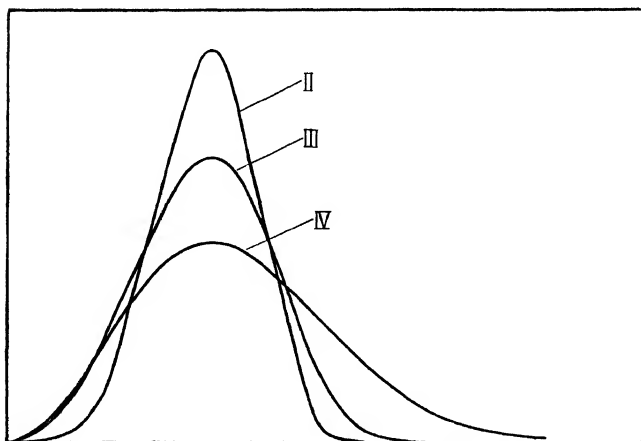


FIG. 23. II  $dN/N = A \cdot \exp(-BU^4) \cdot U^4 \cdot dU$ ;  
 III  $dN/N = A \cdot \exp(-BU^4) \cdot U^3 \cdot dU$ ;  
 IV  $dN/N = A \cdot \exp(-BU^2) \cdot U^3 \cdot dU$ .

investigation of the more general expression

$$dN/N = A. \exp (-BU^r).U^p.dU$$

for values of  $r$  and  $p$  in the neighbourhood of 4 and 2 respectively, from which it can be shown that there is a notable difference between  $W_T/W$  and  $W_B/W$  when  $r$  is appreciably different from 4 or  $p$  from 2

The distribution III is in agreement with that arrived at by Druyvesteyn\*, Davydov† and Morse, Allis and Lamar¶, who by making the rather special assumption that collisions are elastic deduced this formula theoretically. It is also supported by the results obtained by Townsend§ and Llewellyn Jones‡ for electrons with somewhat higher energies; these results, however, suggest that the formula III underestimates the small proportion of electrons having velocities considerably greater than the mean. Pidduck has also pointed out that this formula is a special case of the more general result which he derived somewhat earlier||.

It might be expected that the distribution would vary with  $k$ , but the close agreement between the results obtained respectively by Townsend and by Bailey suggests not only that the distribution is independent of  $k$  over a fairly wide range, but also that it is effectively independent of the particular gas, and hence of the elasticity or otherwise of the collisions. From this last conclusion, it will be seen that there is some justification for a wider application of the formulae deduced from theoretical investigations in which it is assumed that all collisions are elastic.

Further evidence that the distribution does not vary markedly from gas to gas is afforded by the results obtained by the method of mixtures described in §2.5; thus, for chlorine (see §2.6), there is a very close agreement between the values of  $k$  determined from observations on mixtures of this gas with such widely-differing gases as helium and carbon dioxide, collisions being effectively elastic over a fairly wide range in helium, and notably inelastic over the same range in carbon dioxide (see §1.7). These particular results also support the conclusion that the distribution does not

\* M. J. Druyvesteyn, *Physica*, **10**, p. 61 (1930), **1**, p. 1003 (1934).

† P. Davydov, *Phys.Zeits.der Sowjetunion*, **8**, p. 59 (1935).

¶ P. M. Morse, W. P. Allis and E. S. Lamar, *Phys Rev.*, **48**, p. 412 (1935).

§ J. S. Townsend, *Phil Mag.*, **9**, p. 1145 (1930); **22**, p. 145 (1936).

‡ F. Llewellyn Jones, *Proc.Phys Soc*, **48**, p. 513 (1936).

|| F. B. Pidduck, *Quart. J. of Math*, **7**, p. 199 (1936); *Proc.Lond.Math.Soc.*, **15** p. 89 (1915).

vary appreciably over a wide range of energies, as Pidduck showed in his earlier paper that for inelastic collisions, the distribution is that corresponding to the value of  $k$  which would be acquired in the same electric field with perfect restitution.

Adopting the distribution III, the correct formulae are those given in the following table; it will be seen that they are not seriously different from those used in Chapters I and II.

Table 16.

Townsend's Method	$k = k_1/1.14.$ $u = 1.15 k^{\frac{1}{2}} \times 10^7.$ $W = 0.94 \frac{Z}{H} \tan \theta.$ $L = \frac{1}{0.83} W \left( \frac{pm}{Ze} \right) u.$ $\lambda = 2.54 W^2 u^{-2}.$
Bailey's Method	$k = k_1/1.14.$ $u = 1.15 k^{\frac{1}{2}} \times 10^7.$ $W = 0.97 \frac{Z}{H_0} k^{\frac{1}{2}}.$ $L = \frac{1}{0.83} W \left( \frac{pm}{Ze} \right) u.$ $\lambda = 2.54 W^2 u^{-2}.$ $h = \frac{1}{0.95} \left( \frac{aLW}{p} \right) u^{-1}.$

It should be noted that the argument used in this section to deduce a probable velocity-distribution holds only for a certain range of electronic energies; thus, the formula for  $W$  given in table 13 for Bailey's method becomes appreciably inaccurate for values of  $k$  less than 5, and the experimental results extend only to values of  $k$  of the order 100.



## IV

### THE RESULTS OBTAINED BY DIFFUSION METHODS

#### 4.1—The Energy of Agitation.

In the present chapter it is proposed to give a summary of the experimental results obtained by the diffusion methods and to comment briefly on some of the more striking features of these results. A more complete discussion of individual gases is given in the original publications, to which reference is made in §4.6.

We begin with the energy factor  $k$ . It is found that this quantity increases with  $Z/p$ ; and that, for the same value of  $Z/p$ , it may vary considerably from gas to gas. For example, the values of  $k$  in the inert gases are notably larger than the corresponding values in the active gases. These points are illustrated by the following results.

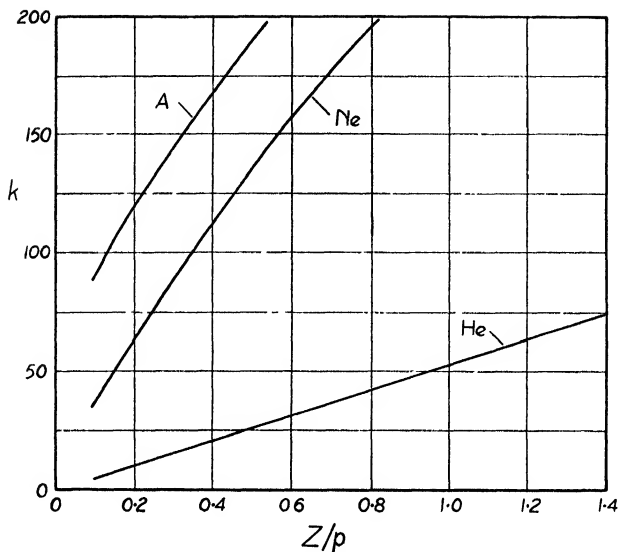
$Z/p$	$k$	
	$A$	$NH_3$
5	310	1.5
10	324	12

Curves showing the variation of  $k$  with  $Z/p$  in a number of gases are shown in figures 24a, b, c and d.

The results for chlorine, bromine and iodine have already been given in figures 13-18 in §2.6.

#### 4.2—The Drift Velocity.

For any gas, the drift velocity, like  $k$ , increases with  $Z/p$ ; it is considerably less than  $u$  in the ranges here considered, but approaches  $u$  for higher values of  $Z/p$ .

FIG. 24a. ( $Z/p, k$ ) curves for argon, helium and neon.

The experimental results show that, unlike  $k$ , the value of  $W$  for a given value of  $Z/p$  does not vary greatly from gas to gas, as is illustrated by the typical results given in table 2 in §1.5. A remarkable difference, however, is shown by the results obtained for argon and for a mixture containing 96 per cent. of argon and 4 per cent. of hydrogen, the higher values of  $W$  in the mixture being due principally to the effect of hydrogen in reducing the velocity of agitation.

Figures 25 a, b, c and d give the curves ( $Z/p, W$ ) for a number of gases.

### 4.3—The Mean Free Path.

The experiments described previously show that  $L$  may vary considerably with the electronic velocity. Chlorine furnishes a most striking example, as  $L$ ,  $\lambda$  and  $h$  for this gas vary by large factors over the range studied; and in such a case the variation of the mean free path with the agitational velocity may introduce an appreciable error in the formulae used.

In general, the quantity  $L$  varies widely with the gas ; the longest mean free path has been observed in argon and the shortest in chlorine, the values being 1.6 cm and  $5 \times 10^{-4}$  cm respectively.

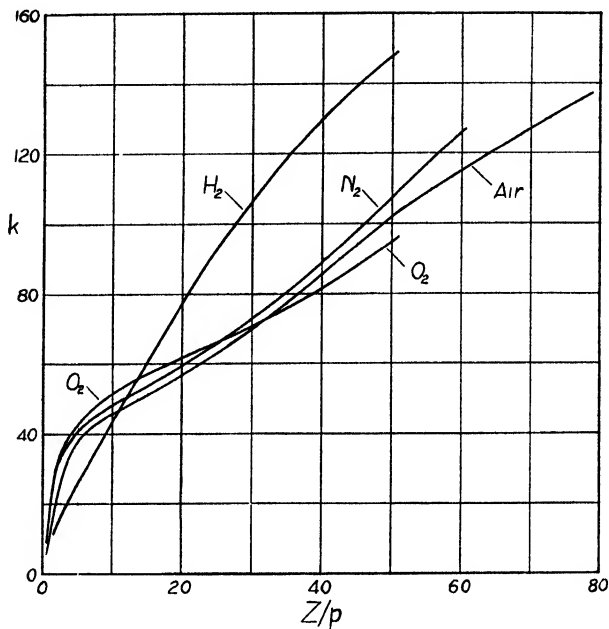


FIG. 24b ( $Z/p, k$ ) curves for hydrogen, air, nitrogen and oxygen

The  $(L, u)$  curves for various gases may be grouped in two main classes, the first having a minimum and the second a maximum in the range studied ; to the first class belong air, hydrogen, nitrogen, argon, carbon monoxide, helium, neon, nitric oxide and oxygen ; to the second belong argon, pentane, ammonia, water vapour, nitrous oxide, carbon dioxide, chlorine, bromine, iodine and ethylene.

The first gases investigated showed a distinct minimum value of  $L$ , a phenomenon commonly known as the Ramsauer effect\*.

\*It should be noted that in their original publications of this phenomenon, simultaneously but independently, Ramsauer stated that it was true only for argon while Townsend and Bailey stated it to be true for all the three gases investigated by them.

Attempts to explain this behaviour on the classical theory were made by Hund† and by Zwicky‡, but it was not until 1929 that a satisfactory theory was given by Holtsmark\*, who used wave-mechanical reasoning to explain the results obtained for argon and krypton. Holtsmark's work has been extended to a number of gases by Allis and Morse||. A further investigation has been made by Voss¶.

Curves showing  $L$  as a function of  $u$  are given in figures 26 a, b, c and d.

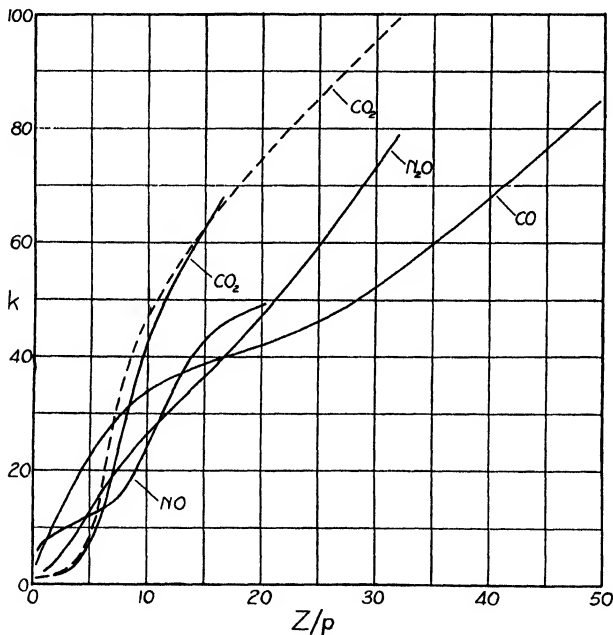


FIG 24c. ( $Z/p, k$ ) curves for nitric oxide, nitrous oxide, carbon monoxide and carbon dioxide. The broken curve represents Skinker's results for carbon dioxide, and the full curve Rudd's results.

† F. Hund, *Zeits.f.Phys.*, **13**, p. 241 (1923).

‡ F. Zwicky, *Phys.Zeits.*, **24**, p. 171 (1923).

\* J. Holtsmark, *Zeits.f.Phys.*, **55**, p. 437 (1929); **66**, p. 49 (1930). See F. L. Arnot, "Collision Processes in Gases," 1933, pp. 55 and 72, and N. F. Mott and H. S. W. Massey, "The Theory of Atomic Collisions," 1933.

|| W. P. Allis and P. M. Morse, *Zeits.f.Phys.*, **70**, p. 567 (1931).

¶ W. Voss, *Zeits.f.Phys.*, **83**, p. 581 (1933).

#### 4.4—The Mean Energy Lost at a Collision.

It has already been pointed out in §1.7 that  $\lambda$  usually varies markedly with the velocity of agitation, and from gas to gas. In carbon dioxide, for example,  $\lambda$  varies between  $2.3 \times 10^{-4}$  and  $5 \times 10^{-2}$  over the range studied, and there are similar variations in the halogens; the smallest value of  $\lambda$  so far observed is for argon, and the largest for nitrous oxide, these values being  $1.5 \times 10^{-5}$  and  $1.5 \times 10^{-1}$  respectively.

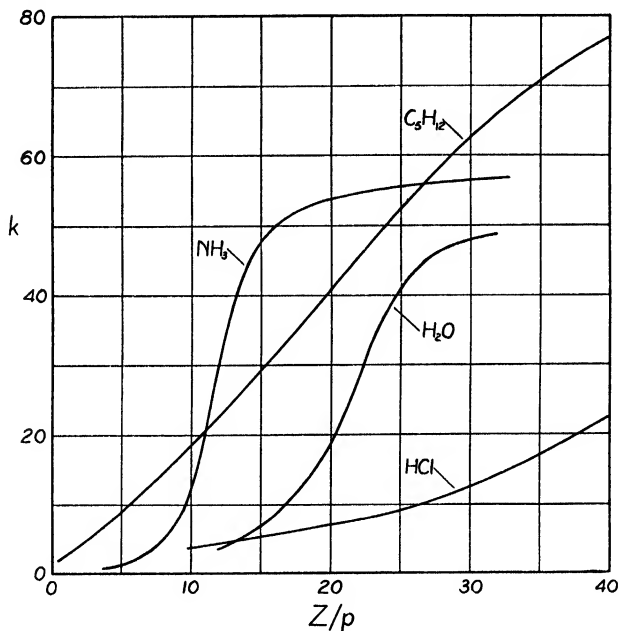


FIG. 24d.  $(Z/p, k)$  curves for pentane, ammonia, water vapour and hydrogen chloride.

It has also been shown that, in a number of gases, collisions between electrons and molecules are almost perfectly elastic for low values of  $Z/p$  (see table 4, §1.7); such gases are air, helium, argon, nitrogen and hydrogen.

In many cases it has been found that there is a definite relation between the light-absorption and  $(\lambda, u)$  curves for a gas,

$\lambda$  being large at values of  $u$  corresponding to wave-lengths at which the light-absorption is large, and small at those values corresponding to regions in which the light-absorption is small. This behaviour is illustrated by the results for the halogens given in table 11, §2.6. A number of other gases also exhibit this relationship, as is shown by the following table.

Table 17.

Gas	$\lambda_{max}$ occurs at $u =$	Maximum in Absorption Curve corresponds to $u =$
$NH_3$	$2.0 \times 10^7$	$2.5 \times 10^7$
$C_2H_4$	$2.3 \times 10^7$	$2.3 \times 10^7$
$N_2O$	$3.0 \times 10^7$	$3.2 \times 10^7$
$CO$	$3.4 \times 10^7$	$3.2 \times 10^7$
$CO_2$	$3.8 \times 10^7$	$3.2 \times 10^7$

Nitric oxide presents an interesting case, the behaviour being somewhat anomalous in that the peak in the  $(\lambda, u)$  curve corresponds, not to the fundamental vibration absorption band at  $5.3\mu$ , but to the weaker harmonic at  $2.6\mu$ .

In the  $(\lambda, u)$  curve for nitrous oxide there occurs a second, smaller maximum at  $u = 7 \times 10^7$  cm/sec, this velocity corresponding fairly closely to the value 30,000 calories per gramme molecule given\* for the energy of activation of the molecule.

Curves showing the variation of  $\lambda$  with  $u$  are given in figures 27 a, b, c and d.

#### 4.5—The Attachment Coefficient and the Probability of Attachment.

Early experiments at Oxford indicated that appreciably no negative ions were formed by attachment in argon, helium, neon, hydrogen, nitrogen, carbon dioxide and carbon monoxide.

\* Hinshelwood and Burk, *Proc. Roy Soc., A*, **106**, p. 284 (1924). Volmer and Kimmervov, *Zetts.f. Phys. Chem* B, **9**, p. 141 (1930).

When negative ions were present, a transverse magnetic field of a few hundred gauss would not deflect the entire stream from the centre collector-electrode.

The methods described in chapter 2 made possible the determination of the attachment coefficient and the probability of attachment for gases in which negative ions are formed.

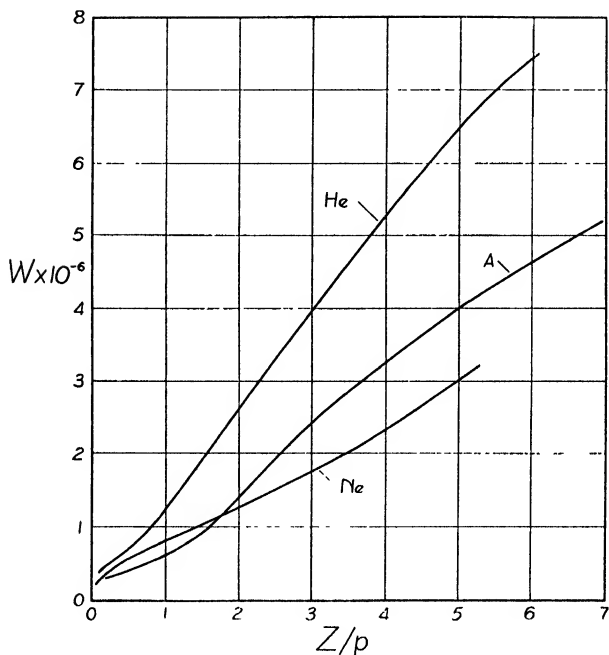


FIG. 25a. ( $Z/p, W$ ) curves for argon, helium and neon

Curves showing the variation of  $a/p$  with  $Z/p$  in a number of gases are given in figures 28 a and b. Negative ions are also formed in nitric oxide, but the experimental conditions for this gas were such that accurate values of  $a/p$  (and hence of  $h$ ) could not be obtained; however, it was found that  $h$  diminished considerably as  $u$  increased.

For the gases investigated at Sydney it was found that  $h$  differs greatly from gas to gas, the variation of  $h$  with  $u$  in each case being considerable; for these gases it was also found that

there is usually a close correspondence between the variations in the  $(h,u)$  and  $(L,u)$  curves.

The theory has been put forward that there may be an association between  $h$  and the electric moment  $\mu$  of a molecule; such a relation is supported by some of the earlier results\* but appears unlikely in the light of the results obtained for the halogens. A more probable relation is that between the variation of  $L$  and  $h$  with  $u$  and the magnetic properties of the molecule†; in certain gases which are paramagnetic,  $L$  and  $h$  diminish on the whole as  $u$  increases, while both quantities exhibit a general tendency to increase with  $u$  in a number which are diamagnetic.

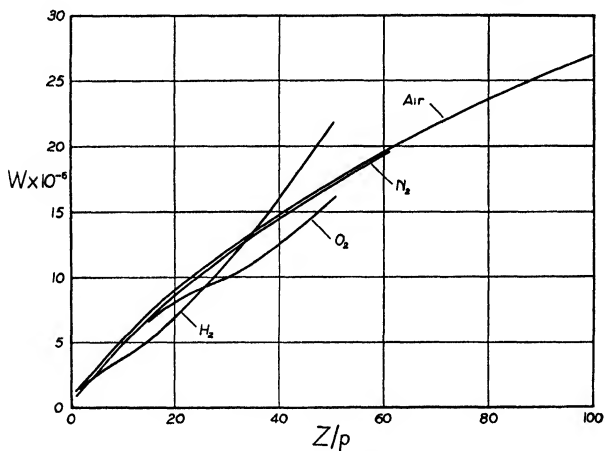


FIG. 25b  $(Z/p, W)$  curves for hydrogen, air, nitrogen and oxygen.

Curves showing  $h$  as a function of  $u$  are given in figures 29 a and b. It will be seen that, in most cases,  $h$  rises from small values up to a maximum and then falls away.

In table 18 are given the least and greatest values of  $h$  recorded for a number of gases.

For some gases there is a rough agreement between the energy of dissociation of the molecule and the electronic energy at which  $h$  has a maximum value; this would suggest that, in these cases,

\* See V. A. Bailey and A. J. Higgs, *Phil.Mag.*, 7, p. 277 (1929).

† V. A. Bailey and J. M. Somerville, *Phil.Mag.*, 17, p. 1169 (1934).



Table 18.

Gas	Greatest values of $h$	Least values of $h$
$A, Ne, He, N_2,$ $H_2, CO_2, CO$ $C_5H_{12}$	0 $1.2 \times 10^{-5*}$	0 $1.8 \times 10^{-6}$
$O_2$	$1.8 \times 10^{-4}$	0
$N_2O$	$7.3 \times 10^{-5}$	0
$NH_3$	$4.1 \times 10^{-4}$	0
$HCl$	$4.7 \times 10^{-4}$	$4.0 \times 10^{-5}\dagger$
$H_2O$	$5.0 \times 10^{-4*}$	$6.0 \times 10^{-6}\dagger$
$Cl_2$	$1.4 \times 10^{-3}$	0
$Br_2$	$1.6 \times 10^{-3}$	0
$I_2$	$6.4 \times 10^{-3}$	$1.0 \times 10^{-3}\dagger$

\*  $h$  still rising.  
†  $h$  still falling.

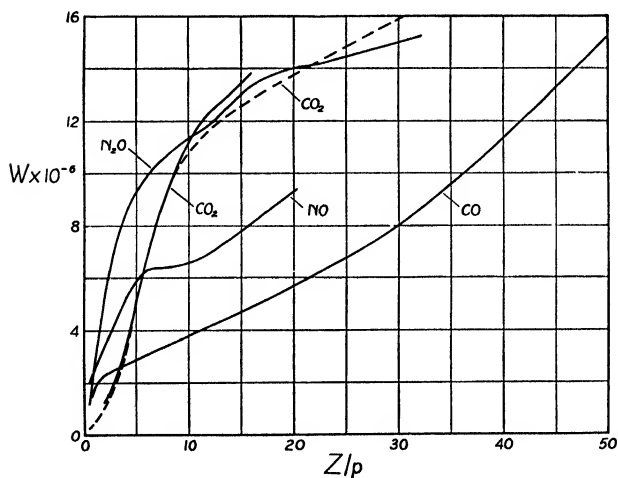


FIG. 25c.  $(Z/p, W)$  curves for nitric oxide, nitrous oxide, carbon monoxide and carbon dioxide. The broken curve represents Skinker's results for carbon dioxide, and the full curve Rudd's results.

the formation of negative ions is bound up with the dissociation of the molecule, the electrons attaching themselves to atoms.

Table 19.

Gas	$h_{max}$ occurs at $u =$	Energy of Dissociation is equivalent to $u =$
$Cl_2$	$7.6 \times 10^7$	$9.3 \times 10^{7*}$
$Br_2$	$9.9 \times 10^7$	$8.4 \times 10^{7*}$
$I_2$	$8.6 \times 10^7$	$7.2 \times 10^{7*}$
$N_2O$	$7.5 \times 10^7$	$6.8 \times 10^{7\dagger}$
$NH_3$	$8.5 \times 10^7$	$10.3 \times 10^{7¶}$

\* See table 12, §2.6.  
 † Hinshelwood and Burk, *Proc Roy.Soc*, A, **106**, p. 284 (1924), Volmer and Kummerov, *Zeits f Phys, Chem* B, **9**, p. 141 (1930).  
 ¶ N. E. Bradbury, *Journ Chem.Phys*, **2**, p. 835 (1934)

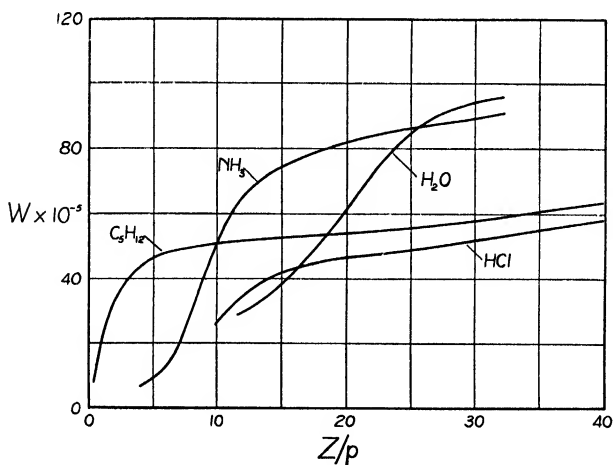


FIG. 25d  $(Z/p, W)$  curves for pentane, ammonia, water vapour and hydrogen chloride.

#### 4.6—Summary of Experimental Results.

In the present section, the results given by means of curves in the preceding sections are summarized in the form of tables, the various quantities being presented as functions of  $Z/p$ .

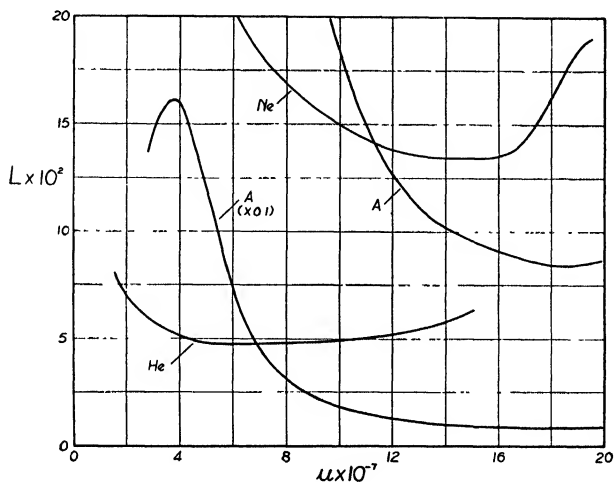


FIG. 26a. ( $L, u$ ) curves for argon, helium and neon.

It should be noted that the results given in this chapter have been calculated by means of the formulae listed in table 14, §3.5. If the distribution suggested by the evidence quoted in that section be adopted, then suitable correction factors are those given in column III of table 15. Work published prior to 1925 made use of Townsend's methods, and the work published later was done by means of the methods developed at Sydney.

#### Notation.

- $p$  = pressure of gas, in mm of mercury.
- $Z$  = electric intensity, in volts/cm.
- $k$  = mean energy of agitation of an electron in terms of the mean energy of agitation of a molecule at 15°C.
- $u$  = the mean velocity of agitation of an electron, in cm/sec.

- $W$  = the drift velocity of an electron parallel to the electric field, in cm/sec.
- $L$  = the mean free path of an electron in the gas at 1 mm pressure, in cm.
- $\lambda$  = the mean proportion of its own energy lost by an electron at a collision with a gas-molecule.
- $\alpha$  = probability of attachment of an electron to a molecule per unit length of its motion in a direction parallel to  $Z$ .
- $h$  = the probability of an electron becoming attached to the molecule with which it collides.

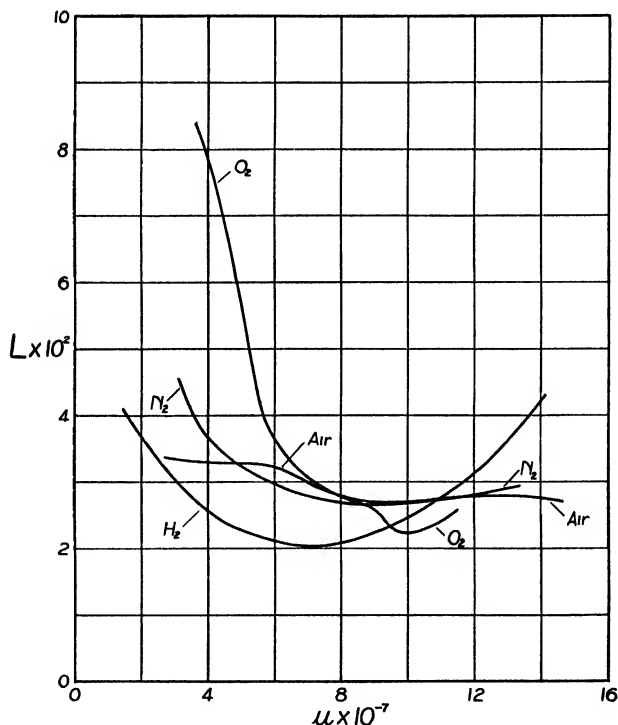


FIG. 26b.  $(L, \mu)$  curves for hydrogen, air, nitrogen and oxygen.

## HELIUM

J. S. Townsend and V. A. Bailey, *Phil. Mag.*, **46**, p. 657 (1923).

$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^4$
0.013	1.77	1.53	1.11	9.14	1.30
0.02	2.12	1.68	1.33	7.8	1.56
0.05	3.68	2.12	2.14	6.6	2.3
0.1	6.2	2.87	2.96	5.95	2.6
0.2	11.3	3.87	3.93	5.3	2.5
0.5	27	5.96	5.74	4.8	2.3
1	53	8.4	8.25	4.85	2.4
2	105	11.8	12.7	5.25	2.85
3	137	13.5	17.5	5.5	4.15
4	152	14.2	23.5	5.85	6.75
5	172	15.1	30.2	6.4	9.8

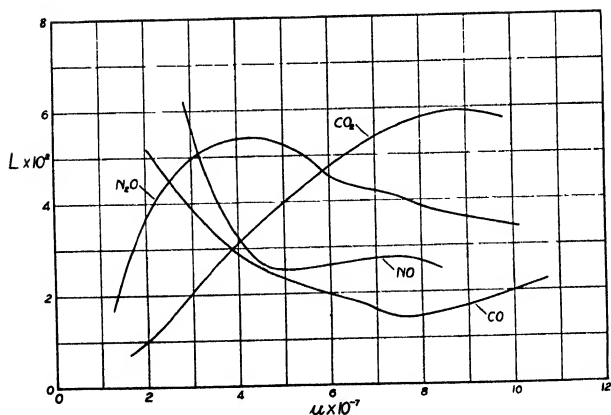


FIG. 26c. ( $L, u$ ) curves for nitric oxide, nitrous oxide, carbon monoxide and carbon dioxide.

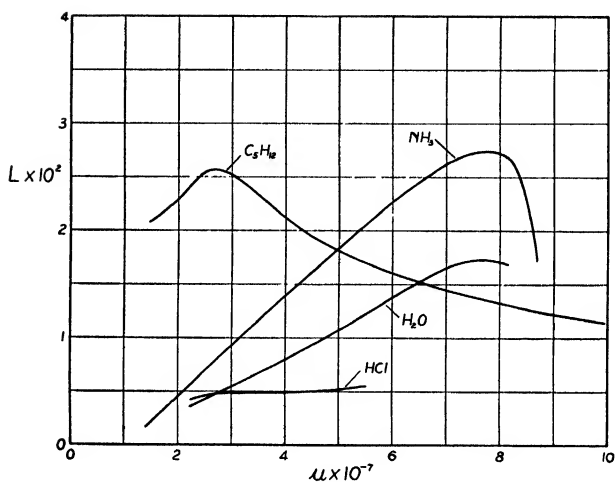
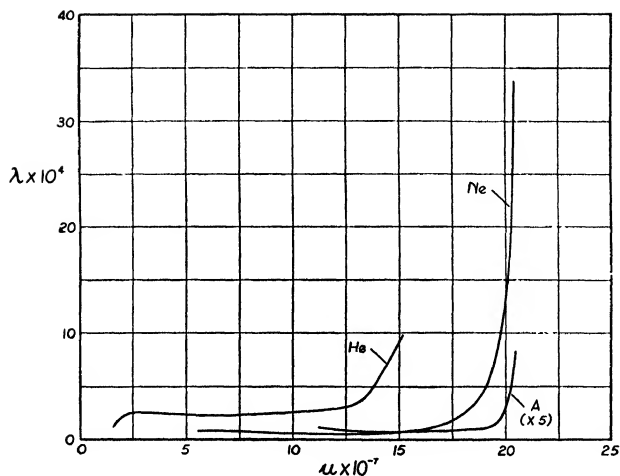


FIG 26d ( $L, u$ ) curves for pentane, ammonia, water vapour and hydrogen chloride

NEON (containing one per cent. of Helium)

V. A. Bailey, *Phil. Mag.*, **47**, p. 379 (1924).

$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^5$
0.06	23.5	5.58	3.3	21.5	8.6
0.1	34.5	6.75	3.95	18.7	8.4
0.2	62	9.05	5.0	15.8	7.5
0.4	114	12.3	6.35	13.7	6.6
0.6	158	14.5	7.95	13.4	7.4
0.8	194	16.0	9.65	13.5	9.0
1.2	235	17.6	15.0	15.4	18
2	275	19.1	27.0	18.6	49
4	308	20.2	53.0	18.7	170
6	316	20.4	74.5	17.7	330

FIG. 27a  $(\lambda, u)$  curves for argon, helium and neon

## ARGON\*

J. S. Townsend and V. A. Bailey, *Phil. Mag.*, **44**, p. 1033 (1922).

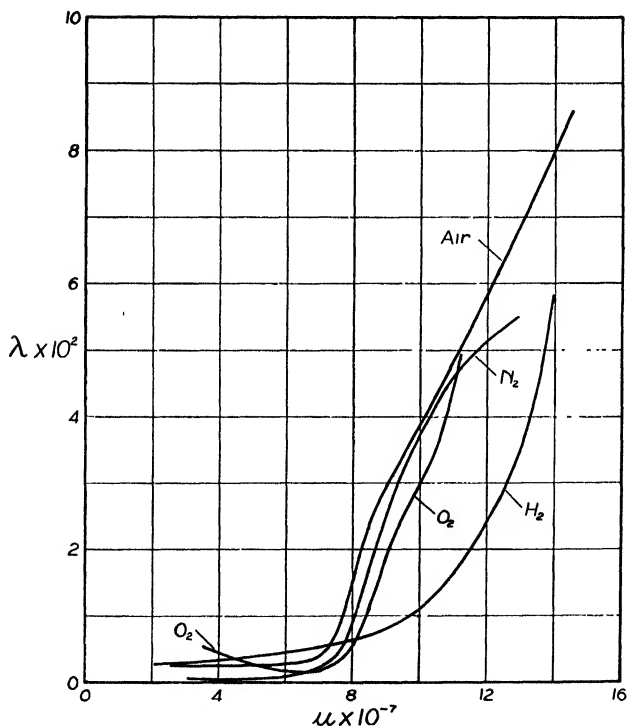
$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^5$
0.125	100	11.5	3.1	20	1.79
0.195	120	12.6	3.25	14.7	1.64
0.355	160	14.5	3.6	10.3	1.52
0.525	200	16.3	4.15	9.0	1.60
0.71	240	17.8	4.85	8.5	1.82
0.95	280	19.3	6.0	8.5	2.38
1.25	320	20.6	7.7	8.9	3.45
5	310	20.2	40	11.3	9.7
10	324	20.7	65	9.4	24.3
15	324	20.7	82	7.9	38.6

\*The results for a mixture containing 96 per cent argon and 4 per cent. hydrogen are given in the same publication and also in Townsend's "Motion of Electrons in Gases" (Oxford, 1925).

## HYDROGEN

J. S. Townsend and V. A. Bailey, *Phil.Mag.*, **42**, p. 873 (1921).

$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^4$
0.25	3.1	2.02	6.5	3.64	26
0.5	5.4	2.62	9.0	3.25	29
1	9.3	3.5	11.9	2.86	28.5
2	15	4.3	16	2.39	34
5	26.4	5.9	25.5	2.14	46
10	44	7.62	38	2.05	62
20	78	10.15	70	2.5	117
40	130	13.1	160	3.67	368
50	148	14.0	217	4.2	590

FIG. 27b)  $(\lambda, u)$  curves for hydrogen, air, nitrogen and oxygen.



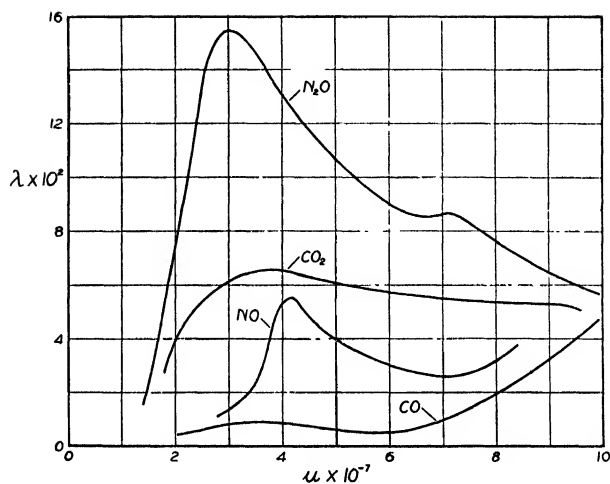
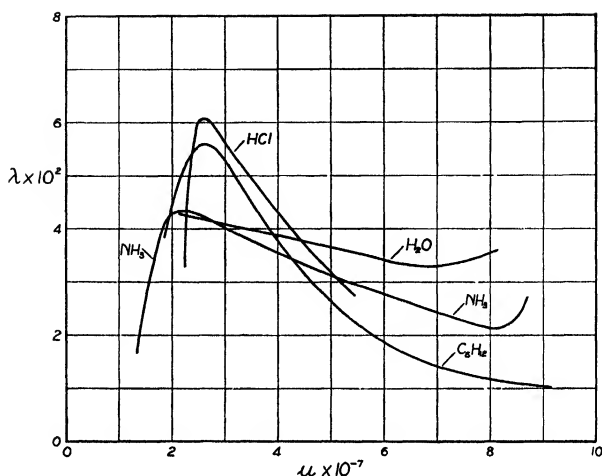


FIG 27c.  $(\lambda, u)$  curves for nitric oxide, nitrous oxide, carbon monoxide and carbon dioxide.

### NITROGEN

J. S. Townsend and V. A. Bailey, *Phil. Mag.*, **42**, p. 873 (1921).

$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^4$
0.25	7.5	3.15	5.15	4.50	6.5
0.5	13.0	4.14	6.2	3.55	5.5
1	21.5	5.35	8.7	3.20	6.5
2	30.5	6.35	13.1	2.88	10.3
3	35.5	6.85	17.8	2.82	16.5
5	41.3	7.4	27	2.77	33
10	48.5	8.0	48.5	2.69	90
20	59.5	8.85	86	2.66	234
40	89	10.8	146	2.75	448
60	126	12.9	193	2.89	550

FIG. 27d.  $(\lambda, u)$  curves for pentane, ammonia, water vapour and hydrogen chloride

## OXYGEN\*

R. H. Healey and C. B. Kirkpatrick, in Sydney, 1939.

$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^4$	$\frac{\alpha}{p} \times 10^2$	$h \times 10^5$
0.25	5.5	2.7	13.3	10.0	60	2.1	10.4
0.5	9.5	3.55	16.1	7.9	51	2.0	7.25
1	19	5.01	16.3	5.66	26.0	1.2	2.2
2	32	6.5	16.9	3.80	15.5	—	—
5	43	7.54	27.3	2.86	32.4	4.7	5.2
10	52	8.29	49.5	2.86	88	9.7	16.7
15	57.5	8.71	67.0	2.71	145	8.2	17.2
20	62	9.05	81.5	2.57	199	3.0	7.0
30	71	9.7	99.5	2.23	260	0	0
50	95	11.2	159	2.47	494	0	0

\* Investigated previously by J. S. Townsend and V. A. Bailey (*Phil.Mag.*, 42, p. 873, 1921) and by H. L. Brose (*Phil.Mag.*, 50, p. 536, 1925).

## AIR

(i) J. S. Townsend and H. T. Tizard, *Proc. Roy. Soc. A.*, **88**, p. 336 (1913).

$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^4$
0.5	5.7	2.7	9	3.37	26
1	11	3.8	12.5	3.30	26
2	22	5.4	17.5	3.28	26
5	38	7.1	30	2.96	43
10	46	7.8	52	2.82	113
20	57	8.7	90	2.71	260
50	102	11.6	173	2.78	550
100	160	14.5	270	2.72	860

(ii) V. A. Bailey, *Phil. Mag.*, **50**, p. 825 (1925).

$Z/p$	$k$	$u \times 10^{-7}$	$(a/p) \times 10^3$	$h \times 10^{6*}$
0.5	8.3	3.3	2.9	3.3
1	15.2	4.5	1.8	2.0
2.0	27.0	6.0	0.65	0.7
2.5	32.5	6.6	0.4	0.4

## CHLORINE

V. A. Bailey and R. H. Healey, *Phil. Mag.*, **19**, p. 725 (1935).

$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^4$	$a/p$	$h \times 10^3$
10	41.0	7.4	76.0	3.80	260	0.34	1.40
15	57.6	8.7	91.6	3.40	270	0.27	1.05
20	65.0	9.3	90.8	2.70	230	0.26	0.74
25	69.7	9.6	91.0	2.30	220	0.26	0.56
30	73.0	9.8	91.6	2.15	218	0.25	0.46
50	80.8	10.3	101.5	1.60	230	0.15	0.24
80	92.0	11.0	137.0	1.30	370	0.0	0.0

\* The probability of attachment  $h$  was calculated by means of the values of  $W$  given by Townsend and Tizard.

## BROMINE

J. E. Bailey, R. E. B. Makinson and J. M. Somerville, *Phil. Mag.*, **24**, p. 177 (1937).

$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^4$	$\alpha/p$	$h \times 10^3$
4	40.0	7.3	—	1.65	4	2.50	0.84
6	55.5	8.6	—	2.70	30	1.50	1.44
10	69.0	9.6	52.0	3.65	75	0.55	1.20
15	75.4	10.0	68.0	2.60	100	0.40	0.60
20	77.8	10.1	74.4	2.45	105	0.28	0.50
30	84.8	10.6	80.0	1.90	140	0.15	—
50	90.6	10.9	91.0	1.60	180	0.10	—
70	91.0	11.0	106.0	1.55	200	0.09	—

## IODINE

R. H. Healey, *Phil. Mag.*, **26**, p. 940 (1938).

$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^4$	$\alpha/p$	$h \times 10^4$
10	18.0	4.9	24.6	0.80	62	—	1.0
15	32.0	6.5	39.0	1.17	92	2.55	1.7
20	51.0	8.2	55.0	1.60	103	5.85	6.0
25	73.0	9.8	70.2	2.09	144	2.30	3.8
30	82.6	10.7	81.2	1.80	147	1.30	1.4
40	91.1	11.0	84.8	1.62	148	—	—
50	97.3	11.4	92.0	1.48	159	—	—

## CARBON MONOXIDE

M. F. Skinner and J. V. White, *Phil. Mag.*, **46**, p. 630 (1923).

$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^4$
0.25	3.2	2.06	9.0	5.14	46.9
0.5	4.8	2.52	13.0	4.5	65.5
1	7.0	3.05	18.0	3.8	86
2	11.4	3.82	23.3	3.04	89.1
5	22.7	5.48	28.5	2.16	52.8
10	34	6.7	38	1.76	79
20	42	7.45	57	1.47	144
30	52	8.3	80	1.53	229
50	86	10.7	152	2.24	500

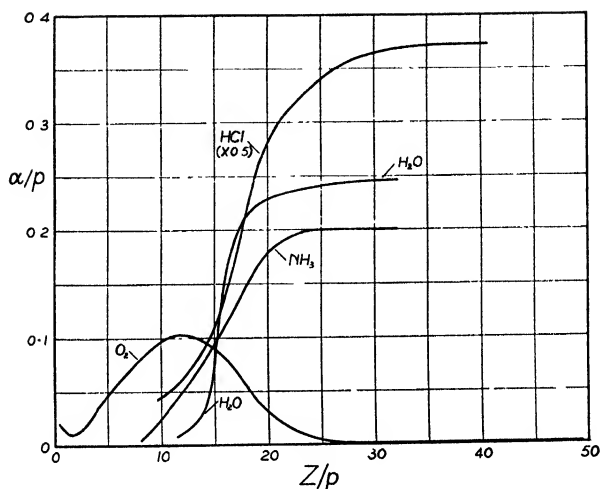


FIG. 28a. ( $Z/p, \alpha/p$ ) curves for ammonia, water vapour, hydrogen chloride and oxygen.

### NITRIC OXIDE†

V. A. Bailey and J. M. Somerville, *Phil. Mag.*, **17**, p. 1169 (1934).

$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^4$
0.5	6.2	2.9	20.2	6.0	130
1	7.7	3.2	25.1	5.2	160
2	9.1	3.5	34.0	4.0	240
3	10.3	3.7	43.0	3.8	340
5	12.3	4.0	58.6	3.2	530
8	16.6	4.7	64.0	2.6	440
12	33	6.6	69.7	2.7	270
16	45	7.7	81.7	2.75	280
20	49	8.0	93.3	2.7	320

†Investigated previously by Skinner and White (*Phil. Mag.*, **46**, p. 360, 1923). Negative ions are formed by attachment, but values of  $\alpha/p$  and  $k$  were not determined accurately.

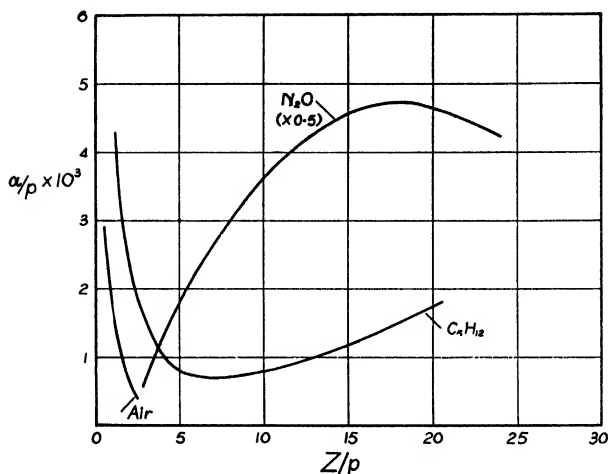


FIG. 28b. ( $Z/p, \alpha/p$ ) curves for pontane, nitrous oxide and air.

### CARBON DIOXIDE

J. B. Rudd, in Sydney. The ( $L, u$ ) and ( $\lambda, u$ ) curves were published in the same communication as the results for nitrous oxide below.

$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^4$
2.0	1.9	1.6	13	0.7	160
3.5	3.0	2.0	26	1.0	400
4.5	5.9	2.8	44	1.8	590
6.0	12	4.0	66	3.1	655
7.5	24	5.6	87	4.5	583
9.0	35	6.8	102	5.3	555
11.0	48	8.0	119	5.8	535
14.0	59	8.8	130	5.9	530
16.0	70	9.6	139	5.8	510

M. F. Skinker, *Phil. Mag.*, **44**, p. 994 (1922).

$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^4$
0.25	1.2	1.2	1.2	0.42	2.34
0.5	1.3	1.3	2.5	0.45	8.95
1	1.5	1.4	5.5	0.54	37.4
2	1.8	1.5	11.8	0.63	144
5	9	3.5	50	2.39	516
10	47	7.9	108	5.91	460
20	75	9.9	138	4.76	472
50	139	13.6	195	3.67	506

### NITROUS OXIDE\*

V. A. Bailey and J. B. Rudd, *Phil. Mag.*, **14**, p. 1033 (1932).

$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^4$	$\frac{\alpha}{p} \times 10^3$	$h \times 10^4$
1	2.4	1.78	25.9	3.21	522	—	—
2	4.1	2.33	53.4	4.32	1290	0.0	0.00
3	6.4	2.91	73.1	4.93	1554	1.3	0.16
5	13.0	4.15	93.2	5.37	1240	3.7	0.45
10	26.4	5.91	113.4	4.58	908	7.3	0.65
16	38.7	7.15	133.7	4.16	860	9.3	0.73
24	57.5	8.72	143.8	3.64	668	8.5	0.51
32	79.0	10.22	152.5	3.39	548	—	—

### WATER VAPOUR

V. A. Bailey and W. E. Duncanson, *Phil. Mag.*, **10**, p. 145 (1930).

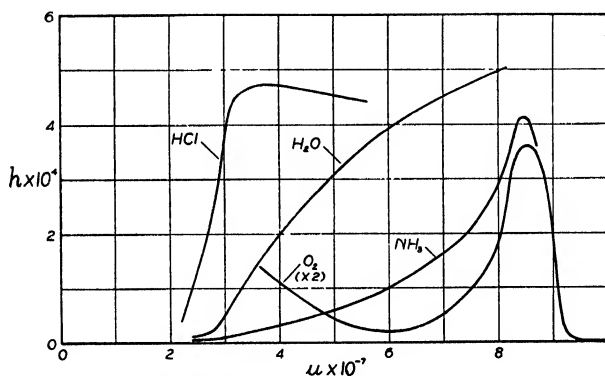
$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^4$	$\alpha/p$	$h \times 10^4$
12	3.78	2.21	30	0.37	423	0.015	0.06
14	5.67	2.72	35	0.48	418	0.03	0.19
16	8.64	3.37	42	0.63	400	0.16	1.3
20	18.9	4.98	62	1.07	369	0.23	3.0
24	37.0	7.00	81	1.65	328	0.24	4.5
32	48.9	8.04	96	1.69	352	0.25	5.0

\* Investigated previously by M. F. Skinker and J. V. White (*Phil. Mag.*, **46**, p. 630, 1923).

## AMMONIA\*

V. A. Bailey and W. E. Duncanson, *Phil. Mag.*, **10**, p. 145 (1930).

$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^4$	$a/p$	$h \times 10^4$
4	1.49	1.40	6.9	0.17	62	—	—
6	1.62	1.43	12.4	0.21	183	—	—
8	4.59	2.49	31	0.67	427	0.006	0.03
10	12.2	4.02	51	1.37	354	0.025	0.32
12	30.0	6.29	65	2.38	261	0.050	1.2
16	50.0	8.12	76	2.70	215	0.115	3.1
24	55.4	8.57	86	2.09	234	0.20	4.1
32	57.0	8.67	92	1.73	273	0.20	3.7

FIG. 29a.  $(h, u)$  curves for ammonia, water vapour, hydrogen chloride and oxygen.

## PENTANE

J. D. McGee and J. C. Jaeger, *Phil. Mag.*, **6**, p. 1107 (1928).

$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^4$	$\frac{a}{p} \times 10^3$	$h \times 10^6$
0.625	1.7	1.5	12.5	2.1	170	—	—
1.25	2.8	1.93	24.2	2.26	390	3.8	13.5
2.5	4.5	2.46	37.0	2.55	560	1.86	6.1
5	8.8	3.51	47.0	2.32	440	0.82	2.5
10	18.4	4.95	51.0	1.77	260	0.80	1.5
20	41.4	7.4	54.5	1.42	130	1.72	1.8
40	77	10.1	63.8	1.13	100	—	—

\* This gas was investigated previously by V. A. Bailey and A. J. Higgs (*Phil. Mag.*, **7**, p. 277, 1929) and by V. A. Bailey and J. D. McGee (*Phil. Mag.*, **6**, p. 1073, 1928).



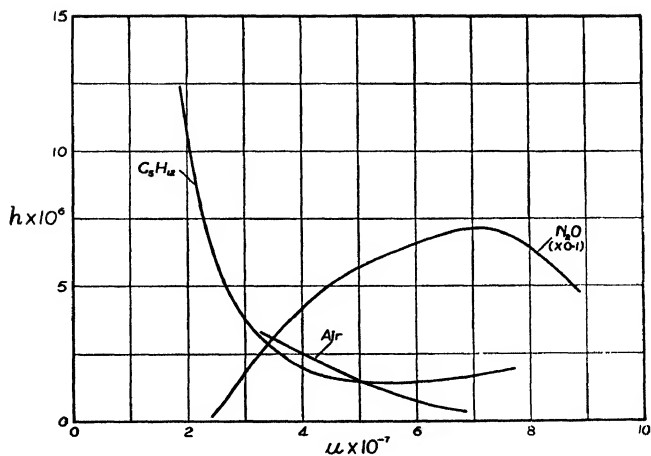


FIG. 29b.  $(h,u)$  curves for pentane, nitrous oxide and air.

### ETHYLENE

J. Bannon and H. L. Brose, *Phil. Mag.*, **6**, p. 817 (1928).

$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^4$
1.26	2.07	1.66	23.3	2.14	488
2.5	5.3	2.65	39.3	2.92	541
4	11.0	3.81	49.6	3.28	416
5	15.0	4.53	54.0	3.42	348
6	19.3	5.05	56.0	3.30	303
10	31.3	6.43	60.3	2.71	217
20	45.3	7.74	67.6	1.83	187
40	64.4	9.23	88.7	1.43	227
60	80.2	10.2	116	1.38	319
80	95.0	11.2	145	1.42	408

## HYDROGEN CHLORIDE\*

V. A. Bailey and W. E. Duncanson, *Phil.Mag.*, **10**, p. 145 (1930).

$Z/p$	$k$	$u \times 10^{-7}$	$W \times 10^{-5}$	$L \times 10^2$	$\lambda \times 10^4$	$a/p$	$h \times 10^4$
10	3.78	2.24	26	0.41	330	0.09	0.4
15	5.40	2.64	42	0.51	600	0.22	1.7
20	7.02	3.04	46.5	0.49	560	0.56	4.1
30	12.2	4.02	52	0.49	420	0.73	4.7
40	22.4	5.46	58	0.56	280	0.74	4.4

\* Investigated previously by V. A. Bailey and A. J. Higgs (*Phil.Mag.*, **7**, p. 277, 1929).

## OTHER METHODS OF INVESTIGATION

## 5.1—Mean Free Paths and Effective Cross-Sections.

In the preceding chapters, an account has been given of the diffusion methods developed by J. S. Townsend and V. A. Bailey ; it is intended in the present chapter to give a brief survey of a number of other techniques, and to discuss the results obtained by them.

We begin by describing the methods used to determine the mean free paths of electrons with regard to gas molecules\*. In all of these, a stream of electrons is passed through the gas, the observation consisting in the measurement of the proportion which suffers neither appreciable energy-loss nor appreciable deflection ; this proportion is clearly given by an expression of the form

$$I/I_0 = e^{-x/d}, \quad \dots\dots\dots(56)$$

where  $I_0$  and  $I$  are respectively the initial and final values of the electron current,  $x$  is the distance traversed by the beam, and  $d$ —for a given gas—is a quantity which is inversely proportional to the pressure and varies with the electronic velocity. Assuming that the gas molecules have a radius  $r$  which is large compared with that of an electron, that the velocity of the electrons is considerably greater than that of the molecules, and that every collision removes the colliding electron from the stream, it is easily shown that

$$d = 1/\pi r^2 N,$$

where  $N$  is the number of molecules in 1 cc of the gas. The quantity  $\pi r^2$  is known as the effective cross-section (“*Wirkungsquerschnitt*”) of the molecule. It is customary, however, to give results in terms of the quantity  $\pi r^2 N/p$  (denoted by  $Q_R$ ) which is known as the total effective-cross-section ; using this notation, equation (56) may be written

$$I/I_0 = e^{-xpQ_R}.$$

\* See C. Ramsauer, *Phys.Zeits.*, **29**, p. 823 (1928) ; E. Bruche, *Ergebnisse d. exakt. Naturwiss.*, **8**, p. 185 (1929) ; R. Kollath, *Phys.Zeits.*, **31**, p. 985 (1930) ; and J. Franck and P. Jordan, *Handbuch d. Phys.*, 1926, **23**, p. 642.

A schematic diagram of an apparatus for the determination of  $Q_R$  is shown in figure 30. Electrons from the source  $Z$  are accelerated to the desired velocity in moving to the slit  $B_1$ ; those

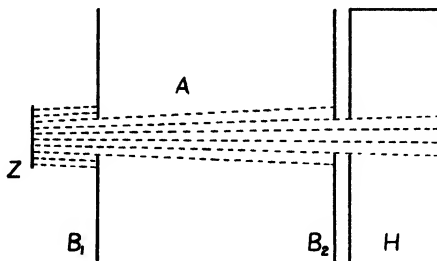


FIG. 30. Schematic diagram of apparatus for determining  $Q_R$ .

which are not deflected when traversing the gas-filled space  $A$  pass through an identical slit into the collecting chamber  $H$ . Let the currents passing through  $B_1$  and  $B_2$  be denoted by  $I_0$  and  $I$  respectively, and let  $x$  be the distance between the slits; the effective cross-section is then given by

$$Q_R = (1/xp) \cdot \log(I_0/I).$$

In practice, in order to eliminate errors such as those caused by an incorrect alignment of the slits, the currents are also measured in vacuo; denoting these corresponding values by  $i_0$  and  $i$ , it will be seen that the cross-section is given by

$$Q_R = (1/xp) [\log(i/i_0) - \log(I/I_0)]. \quad \dots\dots\dots(57)$$

The above equation shows that there is a linear relationship connecting  $\log(I/I_0)$  and  $p$ , this relationship affording a simple experimental check on the apparatus.

The instrument shown in figure 30 is that developed by Lenard\*. This simple arrangement, however, measures only a partial cross-section; for, in the stream passing through  $B_2$ , there still remain electrons which have suffered energy-loss, but which have not been deflected from the stream. One method of overcoming this difficulty

\* P. Lenard, *Ann.d.Phys.*, 2, p. 359 (1900), 8, p. 149 (1902), 12, pp. 449 and 714 (1903).

is that due to Mayer\*, who modified Lenard's original apparatus by applying a retarding field between  $B_2$  and the collecting chamber, the retarding potential being equal to the accelerating potential.

In the methods developed by Ramsauer† and Brode‡, the electrons were constrained to move in a narrow, circular path by means of a magnetic field applied perpendicular to the plane of this path, so that those electrons which suffered energy loss without deflection at a collision were also removed from the stream. In Brode's method, however, as in that of Mayer, a possible error is introduced by the wide, initial velocity-distribution of the electrons coming from the source§. Such an error is obviated by Ramsauer's method, the apparatus being shown in figure 31. Electrons which

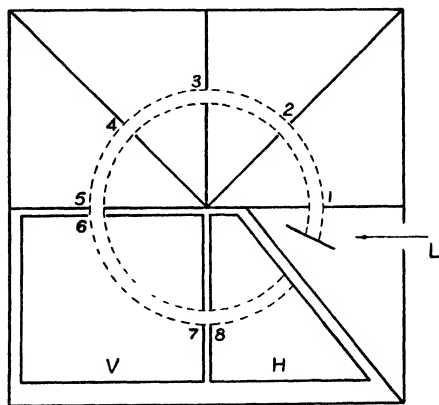


FIG. 31. Ramsauer's apparatus for determining  $Q_R$ .

are deflected or suffer energy loss at a collision are collected by the slit electrodes defining the stream. In this instrument, the slit 5 is to be regarded as the source, so that both the initial and final currents consist of homogeneous streams of electrons, the velocity being defined by the strength of the magnetic field, and the narrow distribution by the width of the slits. The chambers  $V$  and  $H$  correspond to  $A$  and  $H$  in figure 30. A somewhat different

\* H. F. Mayer, *Ann.d.Phys.*, **64**, p. 451 (1921).

† *Ann.d.Phys.*, **64**, p. 513 (1921), **66**, p. 545 (1921).

‡ R. B. Brode, *Phys.Rev.*, **25**, p. 636 (1925).

§ See Kollath, *loc. cit.*

apparatus, also using a magnetic field to obtain a homogeneous stream, has been developed by Rusch\*.

For the low velocity range, the electron current in the instruments described above becomes very small and is therefore difficult to measure. This difficulty is avoided if the stream is not confined to a narrow path, but is allowed to diverge from the source in a cylindrically or spherically symmetric manner. Such instruments have been designed by Brode† and by Rusch‡.

The reciprocal of  $Q_R$  clearly corresponds to a mean free path at 1 mm pressure, but is not necessarily equal to the quantity  $L$  in Townsend's theory, as a collision between an electron and a molecule is defined differently in the two analyses. Townsend defines a collision as an event in which, on the average, an electron loses all its momentum in any specified direction; in the determination of the effective cross-sections, however, a collision is defined as an event in which an electron suffers an appreciable change either in direction of motion or in velocity.

It will be seen from the above definition that the values obtained for  $Q_R$  must depend to some extent upon what is meant by an "appreciable" change, and hence upon the width of the slits. Experiments suggest, however, that below a certain limit the variation of this width does not greatly affect these values‡; this conclusion is supported by the fairly close agreement between the values determined for  $Q_R$  by the various methods described above. It would thus seem that the field of the molecule falls away very rapidly, the molecule behaving much as though it had a definite boundary. Nevertheless, the effective cross-section is to be regarded not as a real cross-section, but rather as a mathematical quantity equal to the cross-section which the molecule would have if, in the collision, it behaved as a solid sphere.

In spite of the difference between the definitions of a collision, corresponding values of  $Q_R$  and  $L^{-1}$  are of the same order, and their variations with the mean electronic energy similar. In general,  $L^{-1}$  is less than  $Q_R$ ; frequently, also, the curves ( $Q_R, u$ ) exhibit sharper maxima than the corresponding ( $L^{-1}, u$ ) curves, this difference being due to the narrower velocity-distributions associated

\* See Kollath, *loc. cit.*

† *Proc. Roy. Soc., A*, **109**, p. 397 (1925).

‡ M. Rusch, *Phys. Zeits.*, **26**, p. 748 (1925).

§ See O. Beeck, *Zeits. f. Phys.*, **61**, p. 251 (1930); **64**, p. 727 (1930); and Kollath, *loc. cit.*, p. 1004.

with the methods used to determine  $Q_R$ . Typical results are shown in figure 32, where the values for  $L^{-1}$  obtained in hydrogen by Townsend and Bailey are compared with the values of  $Q_R$  determined by a number of investigators.

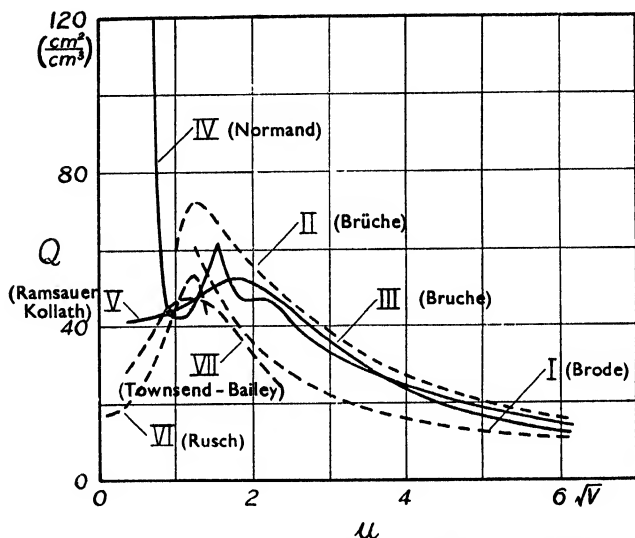


FIG. 32. Comparison of various values for the effective cross-section of electrons in hydrogen.

It might be expected that, for a given gas, there would be a fairly close agreement between the positions of corresponding maxima and minima in the curves  $(Q_R, u)$  and  $(L^{-1}, u)$ . Comparisons have already been given by Kollath and by Brose and Saayman\*. Most of the measurements of  $Q_R$  have been made in the higher velocity range ( $u > 1 \sqrt{\text{volt}}$ ); nevertheless, in the common domain there is a very good agreement between corresponding maxima and minima, as is shown by table 20, where the values of  $u$  are compared at which maxima occur in the curves  $(Q_R, u)$  and  $(L^{-1}, u)$  for a number of gases. In the methods used to determine  $Q_R$ , the velocity  $u$  can be calculated immediately, so that this agreement furnishes further evidence that the diffusion methods of determining the mean energy of agitation are reliable.

\* *Ann.d.Phys.*, **5**, p. 797 (1930).

Table 20.

Gas	Position of ( $Q_T$ ) max.	Position of ( $Q_R$ ) max.
<i>A</i>	3.1 $\sqrt{\text{volts}}$	3.4 $\sqrt{\text{volts}}$
<i>H</i> <sub>2</sub>	1.3	1.5-1.7
<i>N</i> <sub>2</sub>	1.5	1.5
<i>CO</i>	1.4	1.4
<i>N</i> <sub>2</sub> <i>O</i>	1.2 (weak)	1.4
<i>O</i> <sub>2</sub>	1.75	1.5 (weak)
<i>C</i> <sub>2</sub> <i>H</i> <sub>4</sub>	1.7	1.6

### 5.2—Energy Losses at a Collision.

Apart from the ( $\lambda, u$ ) curves obtained for a number of gases by diffusion methods, there is but little information available concerning the energy lost by slow electrons in collisions with gas molecules.

In 1913, Franck and Hertz\* carried out some experiments with the object of comparing the energies of electrons which pass directly from the source to the collector with the energies of electrons which are reflected back in the direction of the source after colliding with gas molecules. In this work, the gas pressure was chosen so that the mean free path was considerably greater than the distance between the two electrodes but less than the distance of the source from the containing walls of the instrument. The distribution of the velocity-components parallel to the electric force was measured by the retarding field method. As an example of the results obtained, figure 33 gives the distribution of these velocity-components for both primary and reflected electrons in helium at a pressure of 0.083 mm, the accelerating potential being 4 volts; curve *I* corresponds to primary electrons, curve *II* to the reflected electrons. It will be seen that the two curves are somewhat similar in shape, the maximum energy attained in each case being approximately equal to the accelerating potential. From this experiment it

\* J. Franck and G. Hertz, *Ber.d.D.Phys.Ges.*, 15, p. 373 (1913). See, also, Franck and Jordan, *Handbuch d.Phys.*, 1926, 23, p. 651.



was therefore concluded that the proportion of its energy lost by a slow electron at a collision with a helium atom is small. The accuracy of the method was not sufficient, however, to decide with certainty that the energy loss is less than several per cent.

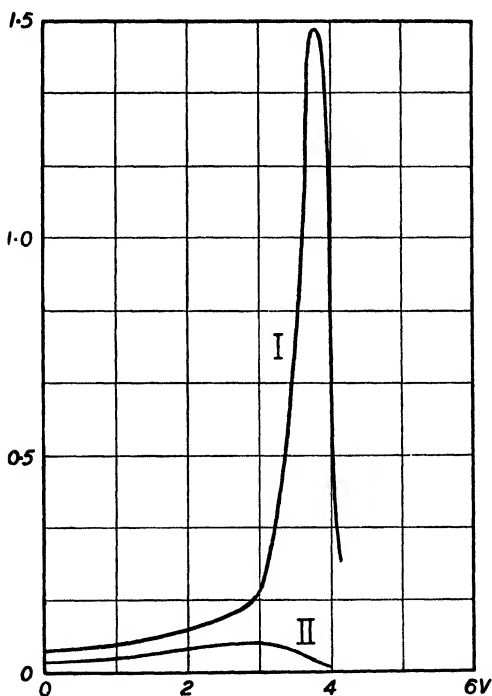


FIG. 33. Comparison of the energies of primary and reflected electrons in helium.  
Curve I corresponds to the primary electrons.  
Curve II corresponds to the reflected electrons.

Similar results were obtained in hydrogen by Baerwald\*. In oxygen, however, it was found that the proportion of reflected electrons was considerably smaller, and that the energies of these electrons were much less than those of the primary electrons (see figure 34). Franck and Hertz put forward the view, supported later by Baerwald, that considerable energy losses would occur in

\* H. Baerwald, *Ann.d.Phys.*, **76**, p 829 (1925)

gases having an electron affinity, and that these energy losses would increase with the electron affinity. Franck and Jordan subsequently discarded this view and suggested that the measured energy losses were only apparent, the presence of negative ions rendering the results difficult of interpretation.

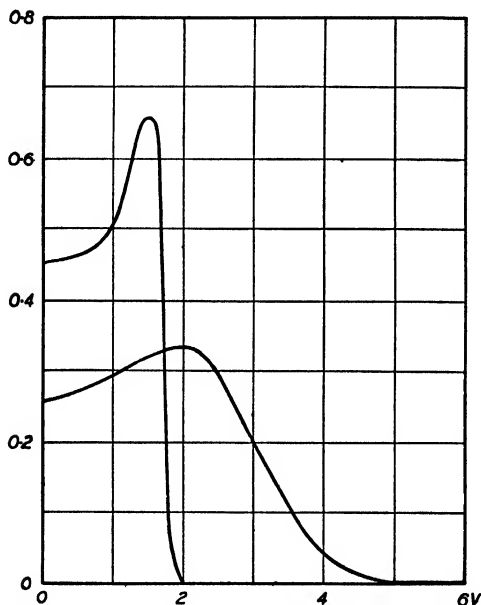


Fig. 34. Comparison of the energies of primary and reflected electrons in oxygen.

The above experiments were only qualitative; in order to obtain more-exact results, Franck and Hertz\* made use of a triode arrangement of filament, grid and plate in which the distance between the grid and plate was small compared with that between the filament and the grid, the construction of the apparatus being such that the latter distance could be varied. Electrons were caused to pass through the gas by applying a positive potential to the grid, and the distribution of the components of velocity in the direction of the field determined for the electrons arriving in the neighbourhood of the grid by applying a varying retarding-

\* *Verh.d.D.Phys.Ges.*, 15, p. 613 (1913).

field between the grid and plate. The results obtained at a pressure of 1.3 mm in helium for an accelerating potential of 18 volts are shown in figure 35 ; curve *I* corresponds to a filament-grid distance

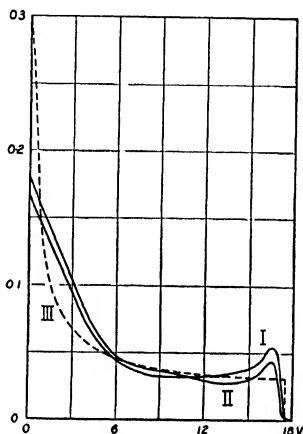


FIG. 35. Velocity distributions of electrons in helium.  
Curve *I* corresponds to a filament-grid distance of 4 mm.  
Curve *II* to a filament-grid distance of 18 mm.  
Curve *III* is calculated by means of Hertz' formula.

of 4 mm, and curve *II* to a distance of 18 mm, this difference being several times the mean free path at the above pressure. Although in the second case the electrons make many more collisions than in the first, the two curves are very similar. The dotted curve *III* was calculated in the following manner on the assumptions that all the electrons arrive at the grid with the same energy (17 volts) and that the directions of motion are equally distributed in all possible directions\* :

Let  $v$  denote the velocity of the electrons at the grid,  $v_x$  the velocity component in the direction counter to the accelerating field, and  $\theta$  the angle between the direction of motion and the field, so that  $\cos \theta = v_x/v$ . The number of electrons whose direction of motion lies between  $\theta$  and  $\theta + d\theta$  is

$$N(\theta).d\theta = N.\sin\theta.d\theta.$$

\* G. Hertz, *Verh.d.D.Phys.Ges.*, 19, p. 268 (1917).

The number of electrons whose velocity component lies between  $v_x$  and  $v_x + dv_x$  is

$$N(v_x).dv_x = \frac{Ndv_x}{v}.$$

Let  $P$  be the potential required to bring to rest an electron of kinetic energy  $\frac{1}{2}mv_x^2$ ; the additional number of electrons brought to rest by increasing the retarding potential from  $P$  to  $P + dP$  is then given by

$$N(P).dP = N \frac{dP}{2\sqrt{PV}},$$

where  $V$  is the energy of the electrons in volts. The curves *I* and *II* are the measured values of  $N(P)/N$  plotted against  $P$ , while curve *III* represents  $1/(2\sqrt{PV})$  plotted against  $P$ , this curve of best fit being obtained for a value of  $V$  equal to 17 volts. The close agreement between these three curves was considered to justify Hertz's assumptions, and to show that the velocity with which the electrons arrived at the grid under the particular conditions was that corresponding to a potential drop of 17 volts, from which it was concluded that slow electrons can make a large number of collisions with helium atoms without losing a considerable portion of their energy.

A number of experiments relating to critical potentials are of interest in connection with the problem of estimating energy losses at a collision. As mentioned above, it was found that, in helium at low pressures, electrons attained velocities appreciably the same as those in vacuo, provided the accelerating potential was not too high. When, however, the accelerating potential in these experiments was raised above a certain critical value such that electrons attained sufficient energy to excite the atoms, the behaviour was very different, as collisions then occurred in which the electrons lost a large proportion of their energies. This effect was clearly demonstrated when a potential of 25 volts was placed on the grid, and the velocity-distribution measured as before\*; in this case it was found that only a very small proportion of the electrons had energies exceeding 6 volts, the first excitation level of the helium atom being 19.8 volts (see figure 36). Further experiments of this type showed that, as the accelerating voltage was

\* See *Handbuch d. Phys.*, 23, p. 656.

steadily increased, the average electron-velocity periodically returned to a low value, the period being equal to the lowest excitation potential.

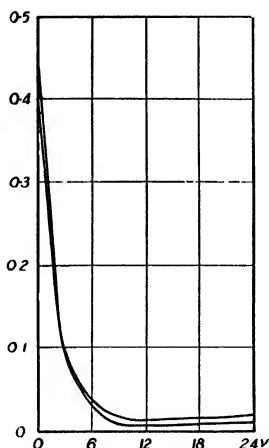


FIG. 36. The energy distribution for electrons in helium, illustrating the effect of the first critical potential.

The experiments mentioned above were carried out at low pressures, so that the electrons made only a few collisions in moving from the filament to the plate. With increased pressures, however, inelastic collisions first occurred for accelerating potentials somewhat higher than the excitation level, because the total energy then lost by an electron in elastic collisions was no longer inappreciable; at higher pressures, too, the periodicity mentioned above became less marked.

It was also found that, if the current-voltage curve were determined in a diode containing the gas, there was an abrupt, periodic discontinuity in the slope of the curve, the periodicity coinciding with that of the average velocity for the same pressure; thus, at low pressures the period corresponded to the first excitation level, increasing with the pressure. From the increase of the period with pressure, the mean energy lost at a collision could be estimated when the average number of collisions made by an electron was known. A series of current-voltage curves for this purpose was obtained by Benade and Compton\*.

\* J. M. Benade and K. T. Compton, *Phys. Rev.*, **11**, p. 184 (1918)

In order to estimate the energy loss at a collision from the various experiments described above, it is necessary to calculate the average number of collisions made by an electron in moving between the electrodes. Franck and Hertz first made use of a formula derived by Hertz† in 1917, a similar formula being derived by Benade and Compton. In 1925, however, Hertz¶ decided that his earlier calculations were in error, as diffusion has then been neglected, and he obtained new formulae which were then applied by Franck and Jordan§ to the results obtained by Franck and Hertz and by Benade and Compton.

Hertz, in his second theory, made the simplifying assumptions that the electrons lose no energy at a collision (so that all the electrons at any point have the same energy) and that the mean free path is constant. Taking the  $z$ -axis parallel to the accelerating field, the following expression was obtained for  $N$ , the number of electrons passing per second through unit surface normal to the  $z$ -axis :

$$N = n\gamma l/3u - (ul/3)dn/dz,$$

where  $n$  is the electron-density,  $\gamma = Ze/m$ ,  $u$  is the velocity of agitation and  $l$  the mean free path. From this result, Hertz showed that the mean number of collisions made by an electron in moving between the filament and the positive electrode, that is, from  $z = 0$  to  $z = a$ , is equal to

$$3a^2/4l^2.$$

Substituting in this formula a value of  $l$  taken from Ramsauer's results, Franck and Jordan estimated  $\lambda$  in helium to lie between  $3 \times 10^{-4}$  and  $1.2 \times 10^{-4}$  from the results of Franck and Hertz, and between  $3 \times 10^{-4}$  and  $8 \times 10^{-4}$  from those given by Benade and Compton. These estimates were supposed to prove that collisions in helium are perfectly elastic for electrons having energies less than the excitation potential\*.

These results are of historical interest but the methods are not precise. In both experiments and theory, the effect of velocity-

† *Verh.d.D.Phys.Ges.*, **19**, p. 268 (1917).

¶ *Zets.f.Phys.*, **32**, p. 298 (1925).

§ *Handbuch d. Phys.*, **23**, pp. 657 and 661.

\* Franck and Jordan, *Handbuch d. Phys.*, **23**, p. 661 : "Danach ist mit der zu erwartenden Genauigkeit, die der Annahme elastischer Stösse gezogene Folgerung bestätigt."

distribution is completely neglected; for example, in the experiment of Franck and Hertz in which 18 volts was applied to the grid, it is not easy to agree that their results establish that the average electron energy at the grid is 17 volts. Further, they appear to neglect the effect of the initial velocities of emission of the electrons, and it is clear that effects due to contact potential could introduce an appreciable error. Moreover, the theory developed by Hertz, which has been used in the calculations, is not entirely satisfactory, as has been shown by Bailey\*.

Finally, it is of interest to compare these results, from which Franck and Jordan deduced that collisions between slow electrons and helium atoms are elastic, with the results shown in table 4 in §1.7. This table shows that values of  $\lambda$  calculated on the assumption of elastic collisions agree very well with the experimental values up to  $k = 80$  (3 volts), and thus provides convincing evidence that, in this range, collisions are elastic.

### 5.3—The Probability of Attachment.

The attachment of electrons to form negative ions has been investigated by Wellish, Loeb, Wahlin, Cravath, Bradbury and Bailey. A number of the methods used are described below.

Early experiments on the mobility of negative ions showed that this quantity was no longer inversely proportional to  $p$  for pressures below a few centimetres. This behaviour was finally traced to the fact that negative ions can be formed in collisions between electrons and molecules; at lower pressures a large number of ions are formed near the collector electrode, so that the apparent mobility is abnormally high, the drift velocity of the electrons being considerably greater than that of the ions.

J. J. Thomson† proposed a theory dealing with the formation of these ions. In this theory it is assumed that out of  $n$  collisions between electrons and a given type of neutral molecule only one will result in an attachment,  $n$  being a constant for the particular type of gas molecule considered.

\* *Zeits.f.Phys.*, **68**, p. 834 (1931). See also Townsend, *Proc.Roy.Soc.*, A, **120**, p. 511 (1928).

† *Phil.Mag.*, **30**, p. 192 (1915).

A short time later, in some experiments on the mobility of negative ions at low pressures, E. M. Wellish† found that the current arriving at the collector electrode consisted partly of negative ions and partly of free electrons. He interpreted these results to mean that the ions were formed in the neighbourhood of the source, where under the particular experimental conditions the electronic energies of emission were relatively high; and concluded that, in the formation of an ion, the electron must have an energy exceeding a certain critical value which he called "the potential energy of ion formation." Some later experiments in dry air\* were considered to support this theory. Both Loeb‡ and Bailey¶, however, have criticized Wellish's interpretation of his results.

Experiments on the formation of negative ions by attachment were carried out by Loeb‡ in order to discriminate between the theories given by Thomson and Wellish. The apparatus used is a modification of that developed by Rutherford for the determination of ionic mobilities. An alternating voltage of square wave-form is applied between the source  $S$  and the collector  $C$ , and a measurement made of the ratio of the current arriving at  $C$  to the current leaving  $S$ . Let  $V$  and  $T$  denote the amplitude and the half-period of the wave, and  $W'$  the drift velocity of the negative ions. It is assumed that only those ions reach  $C$  which are formed at a distance greater than  $x$  from  $S$ , where  $x$  is given by the relation

$$(d - x)/W' = T, \quad \dots\dots\dots(58)$$

$d$  being the distance between  $C$  and  $S$ . The proportion of the electron current arriving at a distance  $x$  from the source is given by

$$I/I_0 = e^{-\alpha x} = \exp[-xhu/(lW)]$$

where  $u$ ,  $l$ ,  $W$ ,  $I$  and  $I_0$  have their usual meanings, and, according to Thomson's theory,  $h = 1/n$ . Substituting the appropriate value for  $x$ , the following equation is then obtained:

$$I/I_0 = \exp[-(d - W'T)hu/(lW)]. \quad \dots\dots\dots(59)$$

Let the mobility of the ions at the particular pressure be  $\mu'$ ; the velocity of drift  $W'$  is then equal to  $\mu'V/d$ . Loeb assumed that

† *Am. Journ. Science*, **39**, p. 583 (1915); **44**, p. 1 (1917); *Phil. Mag.*, **31**, p. 186 (1916); **34**, p. 1 (1917).

\* *Nature*, **128**, p. 547 (1931).

‡ L. B. Loeb, *Phys. Rev.*, **17**, p. 89 (1921).

¶ *Nature*, **129**, p. 166 (1932).



the drift velocity of the electrons is also proportional to the field strength,  $W$  being equal to  $\mu V/d$ , where  $\mu$  is the corresponding "mobility." Assuming that  $l$  equals  $4\sqrt{2}$  times the mean free path of the molecules, that the electrons are in thermal equilibrium with the gas, and taking a known value for  $\mu'$  and assuming a value for  $\mu$  under the particular conditions, he then obtained the equation

$$I/I_0 = \exp \{ -9.9 \times 10^8 h^2 [(7/760)^2/V - 2p/(760N)] \}, \quad (60)$$

where  $N = 1/T$ . Loeb made a large number of observations in air for various values of  $d$ ,  $V$ ,  $p$  and  $N$  in the range  $Z/p < 1$ . The values obtained for  $h$  by substituting in the above equation ranged from  $1.1 \times 10^{-6}$  to  $6.6 \times 10^{-6}$ ; it was considered that these results supported Thomson's theory that  $h$  is independent of  $u$ , the value  $4 \times 10^{-6}$  being chosen as the most probable.

Further experiments of this type were carried out by H. B. Wahlin\*. Making use of Townsend's relation

$$W = 0.815 \frac{Zel}{mu}$$

in equation (59) and assuming that  $W$  is proportional to  $Z/p$ , Wahlin obtained the following equation

$$I/I_0 = \exp \left\{ -\frac{0.815he}{300m\mu^2} [(d.p/760)^2/V - \mu'p/(760N)] \right\}, \quad (61)$$

where  $\mu'$  is the ion mobility and  $\mu$  the "electron mobility" in the gas at 760 mm. In order to evaluate  $\mu$  it was assumed that  $\mu/\mu'$  is the same in all gases, and use was made of an observation by Loeb of  $W$  in nitrogen to decide the value of this ratio. Experiments were carried out at low values of  $Z/p$  in carbon monoxide, ammonia, acetylene, ethylene, ethane, chlorine and ethyl chloride, and the values of  $h$  in each gas computed. Wahlin also made some experiments in air, from which he decided that an increase in the energy of the electrons above that of thermal agitation does not appreciably influence the number of attachments. From these results he concluded that Wellish's theory is untenable and that  $h$  is independent of  $u$ .

The conclusions arrived at by Loeb and Wahlin in support of Thomson's theory have been criticized by Bailey†. Moreover,

\* *Phys.Rev.*, **19**, p. 175 (1922).

† *Phil.Mag.*, **50**, p. 825 (1925).

equation (58) is not accurate, as all the electrons do not leave the source at the instant the accelerating field is applied\*; it might, however, be expected that values of  $a$  calculated by means of this equation would be of the same order of magnitude as those determined by the diffusion methods. The methods used by Loeb and Wahlin to estimate  $W$ , however, are not satisfactory, so that the values which they give for  $h$  can not be regarded as accurate.

The apparatus used by A. M. Cravath† to determine  $a$  is shown in figure 37. A steady electric field is maintained between

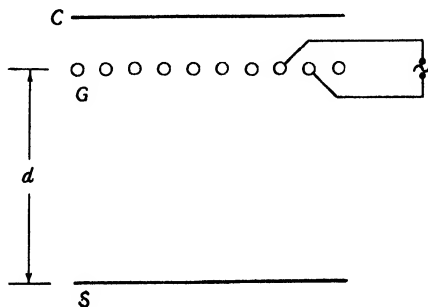


FIG. 37. Schematic diagram of Cravath's apparatus for determining  $a$ .

the source  $S$  and the collector  $C$ , and a high-frequency field applied between adjacent wires of the grid  $G$ . On arriving at the plane of  $G$ , most of the electrons are removed from the stream, while most of the negative ions pass through to the collector  $C$ . Measurements are made of the currents arriving at  $C$  both with the alternating field applied and in the absence of this field; denoting these currents by  $I$  and  $I_0$  respectively, it is clear that the ratio  $I/I_0$  is very nearly equal to  $1 - e^{-ad}$ . The gases investigated were air, oxygen and mixtures of oxygen with water-vapour. In order to estimate  $h$ , Cravath, in effect, makes use of an equation of the form of (26) in §2.3,

$$h = \text{constant} \times \frac{aW^2}{Z};$$

the values used for  $W$  are those given by Townsend and Tizard for

\* Loeb later modified this equation in order to make some allowance for this effect (*Journ. Franck. Inst.*, 197, p. 45, 1924).

† *Phys. Rev.*, 33, p. 605 (1929).

air and by Brose for oxygen. The results obtained by Cravath for values of  $Z/p$  ranging from 0.1 to 1.6 led him to the conclusion that  $h$  varies with  $u$ . In this work some difficulty was encountered in obtaining consistent results.

The method used by N. E. Bradbury\* to determine  $\alpha$  is based on that used previously by Cravath; greater accuracy is attained by using two movable grids,  $G_1$  and  $G_2$ , only one of which is in the stream at any given time. Let  $G_1$  and  $G_2$  be at the respective distances  $d$  and  $d + x$  from the plane of the source  $S$ . For  $G_1$ , let the current arriving at the collector  $C$  be  $I_0$  in the absence of the alternating field, and  $i_1$  when the alternating field is applied; let the corresponding currents for  $G_2$  be  $I_0$  and  $i_2$ . It is then easily shown that

$$1 - e^{-\alpha d} = i_1/I_0$$

and

$$1 - e^{-\alpha(d+x)} = i_2/I_0,$$

whence the following equation for  $\alpha$  is obtained :

$$e^{-\alpha x} = (I_0 - i_2)/(I_0 - i_1).$$

It will be seen that the error arising from an incomplete separation of the electrons and ions is diminished in this method. In order to determine  $h$ , the following equation is used :

$$h = 7.6 \times 10^{-16} \alpha W^2/Z; \dots\dots\dots(62)$$

this equation differs from (26) in §2.3 only in that the factor  $C$  has been taken equal to 0.75 instead of 0.815. The drift velocity is calculated by means of the following equation which relates the photoelectric currents between parallel plates to the drift velocity  $W$  of the electrons and their average initial velocity of emission  $u_0$  :

$$i/I_0 = \sqrt{6\pi} W/(u_0 + \sqrt{6\pi} W), \dots\dots\dots(63)$$

where  $i$  is the current arriving at the collector and  $I_0$  the total emission from the cathode.

The method used by Bradbury to determine  $\alpha$  is satisfactory, but his method of estimating  $W$ , and hence  $h$ , is open to criticism.

\* *Phys.Rev.*, **40**, pp. 508, 524 and 980 (1932); **44**, p. 883 (1933); *Journ. Chem. Phys.*, **2**, p. 827 (1934); Bradbury and H. E. Tatel, *Journ.Chem.Phys.*, **2**, p. 835 (1934).

Equation (63) was suggested by an equation given by Thomson\* relating to the motion of ions :

$$i/I_0 = \sqrt{6\pi} W_1/(u_1 + \sqrt{6\pi}W_1),$$

where  $W_1$  is the drift velocity and  $u_1$  the velocity of agitation of the ions. Thomson's equation was obtained on the assumption that the ion density in the space between the electrodes was constant, and hence cannot be regarded as exact. Bradbury assumes that this relation also holds for electrons, provided the "most probable velocity of emission"  $u_0$  is substituted for the velocity of agitation. It is easily shown that equation (63) can be seriously in error. Moreover, writing this relation in the form

$$I_0/i - 1 = u_0/(\sqrt{6\pi}W),$$

it is clear that the values obtained for  $W$  depend directly on the value assigned to  $u_0$ . Bradbury calculated  $u_0$  from a value given for the work-function of the emitting surface ; and as this quantity depends critically on the condition of the surface, being appreciably affected by the presence of a number of gases, it will be realized that there is a further source of uncertainty in his estimates of the drift velocity. The probability of attachment is proportional to  $W^2$ , so that the corresponding uncertainty in Bradbury's values of  $h$  must be still larger.

The results are given in the form of  $(Z/p, h)$  curves. A number of values of  $h$  obtained by Bradbury are compared in table 21 with corresponding values determined by diffusion methods, and it will be seen that the agreement is only fair.

Table 21.

Gas	$Z/p$	$h$ (Bradbury)	$h$ (diffusion)
Air	2	$3 \times 10^{-6}$	$0.7 \times 10^{-6}$
$NH_3$	20	$4 \times 10^{-3}$	$3.5 \times 10^{-4}$
$H_2O$	16	$2 \times 10^{-4}$	$1.3 \times 10^{-4}$
$N_2O$	20	$1 \times 10^{-3}$	$0.7 \times 10^{-4}$

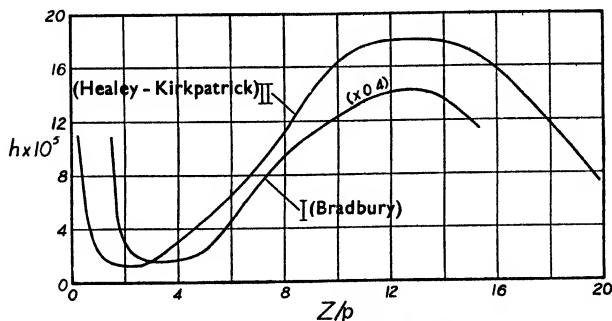
\* "Conduction of Electricity through Gases," 1928, 1, p. 466.

The values of  $a$  obtained by the two methods should agree fairly closely; unfortunately, Bradbury does not give his values of  $a$ . As  $h$  is proportional to  $a/p$ , however, it might be expected that the values of  $a/p$  determined by diffusion experiments and the values of  $h$  given by Bradbury would become appreciable at the same value of  $Z/p$ ; this expectation is borne out by the results shown in table 22.

Table 22.

Gas	$h$ (Bradbury) becomes appreciable at $Z/p =$	$a/p$ (diffusion) becomes appreciable at $Z/p =$
Air	2	2
$NH_3$	8	8
$N_2O$	10	10

It is of interest to compare the  $(Z/p, h)$  curve for oxygen obtained by Bradbury with the corresponding curve determined by Healey and Kirkpatrick using diffusion methods. These two curves, shown in figure 38, are of the same general form, the maximum and minimum values occurring at comparable values of  $Z/p$ ; and although Bradbury's estimates of  $h$  are about twice the others, the agreement must be considered very satisfactory. In addition,

FIG. 38.  $(Z/p, h)$  curves obtained for oxygen.

the  $(Z/p, h)$  curve given by Bradbury for a mixture of chlorine and argon is of roughly the same form as the  $(u, h)$  curve obtained by Bailey and Healey for chlorine, the maximum values of  $h$  being of the same order.

The problem of the formation of negative ions has been considered theoretically. In order that a negative ion should be stable, the electron affinity, that is, the difference in energy between the normal states of the neutral atom or molecule and the corresponding ion, must be positive. In general, the calculation of the electron affinity has not been possible because this quantity represents only a relatively small difference between two energies which cannot be calculated very accurately\*.

In a number of simpler cases, however, it has been possible to estimate the electron affinity. Thus, E. A. Hylleraas† has calculated this quantity for  $H$ , obtaining the value 0.70 volt, and Ta You-Wu‡ has shown that the ion  $He^-$  is unstable. Moreover, it has been shown that  $H_2^-$  is not very stable§, and that  $O_2^-$  and, probably,  $Cl_2^-$ ,  $Br_2^-$  and  $I_2^-$  are stable¶.

Electron affinities for a number of atoms have been determined experimentally by P. P. Sutton and J. E. Mayer\*\* and by Glockler and Calvin††. These experiments show that the atoms  $O$ ,  $F$ ,  $S$ ,  $Cl$ ,  $Br$  and  $I$  have high, positive electron affinities, the value for  $N$  being approximately zero, while  $He$ ,  $Ne$  and  $A$  have large, negative values.

Using a mass spectrograph, O. Tüxen|| found that in discharges in dry air, oxygen, hydrogen, helium, neon and argon the following negative ions were present:  $O^-$ ,  $O_2^-$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $OH^-$  and  $H^-$ . Although the sensitivity of the apparatus was very high, no trace could be detected of negative ions due to nitrogen or to the inert gases.

W. W. Lozier§§ using an apparatus which J. T. Tate and he designed somewhat earlier¶¶, carried out experiments with homo-

\* An excellent account of this problem and the related experimental work has been given by H. S. W. Massey ("Negative Ions," 1938)

† *Zeits.f.Phys.*, **60**, p. 624 (1930).

‡ *Phil.Mag.*, **22**, p. 837 (1936).

§ Eyring, Hirschfelder and Taylor, *Journ.Chem.Phys.*, **4**, p. 479 (1936).

† Massey, *loc. cit.*, pp. 27-30.

\*\* *Journ.Chem.Phys.*, **3**, p. 20 (1935).

†† *Journ.Chem.Phys.*, **3**, p. 771 (1935).

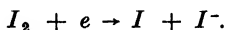
|| *Zeits.f.Phys.*, **103**, p. 463 (1936).

§§ *Phys.Rev.*, **46**, p. 268 (1934).

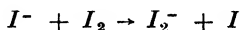
¶¶ *Phys.Rev.*, **39**, p. 254 (1932)

geneous beams of electrons in oxygen and carbon monoxide. The number of ions formed was determined as a function of the electronic energy. In each case the  $O^-$  ion was found to be present at high energies. In oxygen, peaks occurred in the curve at energies of about 7, 16 and 35 volts; the first two peaks were considered to be due to electron capture and the third to dissociation.

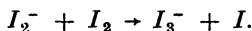
Earlier experiments were carried out in iodine by T. R. Hogness and H. W. Harkness who used a mass spectograph\*. It was found that the ion  $I^-$  was produced by electrons with energies as low as 3 volts, the lowest used in these experiments. The results obtained suggest that the process involved in the formation of this ion is



The ions  $I_2^-$  and  $I_3^-$  were also detected, possible modes of formation being



and

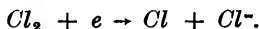


Massey interprets the results obtained by Bailey and by Bradbury for the attachment of electrons in a number of gases as follows :

*HCl.* The process here may be

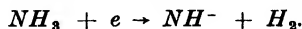


*Cl<sub>2</sub>.* This gas behaves similarly to *HCl*, the probable process being



It is likely that the same mode of formation holds for *Br<sub>2</sub>* and *I<sub>2</sub>*, the results of Hogness and Harkness for *I<sub>2</sub>* lending support to this theory.

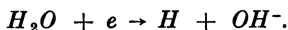
*NH<sub>3</sub>.* Bradbury has shown that the passage of slow electrons through ammonia is accompanied by the formation of a permanent gas, the attachment reaction being



*N<sub>2</sub>O.* Similar to ammonia.

\* *Phys.Rev.*, **32**, p. 784 (1928).

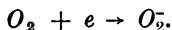
$H_2O$ . In this case there is a very good agreement between the results obtained by the two methods. Attachments begin at mean energies of about 0.1 volt, the number rising steadily as the energy increases. At the highest mean energy occurring in the experiments, about 2 volts, the value of  $h$  is about  $5 \times 10^{-4}$ . Bradbury's method has also been used for very low energies; in this range it is found that the probability of attachment increases when high pressures are used. The process of attachment at high energies is probably



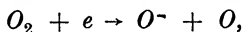
The increase at low energies accompanying an increase in pressure is probably due to polymerization of water vapour approaching condensation.

$H_2S$ . Similar to water vapour, except that there is no attachment for low energy electrons.

$O_2$ . The results obtained by Bradbury (and by Healey and Kirkpatrick) show that there is a maximum and a minimum in the  $(h,u)$  curve. In agreement with Bradbury and Bloch\* it is considered that the lower peak corresponds to the reaction



The second process, however, occurring at energies greater than 1.5 volts, is difficult to interpret. It is not likely that this reaction is



as the energy of dissociation appears to be about 5 volts.

$SO_2$ . Similar to  $O_2$ .

In conclusion, it may be pointed out that the results obtained by the experiments of Bailey and Bradbury are in good agreement with theoretical expectations and with the results obtained by other methods. In these experiments, no attachments have been observed in the inert gases, nor in nitrogen, carbon monoxide and carbon dioxide; while the probability of attachment is high for those gases which have a high electron affinity. Moreover as is shown in Table 19 in §4.5, the maxima in the  $(h,u)$  curves for the gases  $Cl_2$ ,  $Br_2$ ,  $I_2$ ,  $N_2O$  and  $NH_3$  occur at energies close to the dissociation energies of the corresponding molecules, as is to be expected if Massey's interpretations are correct.

\* *Phys.Rev.*, **44**, p. 883 (1933); *Journ.Chem.Phys.*, **2**, p. 827 (1934).



## VI

### THE EFFECT OF ELECTRIC WAVES ON IONISED GASES

#### 6.1—Ionization by Collision.

In a number of the processes discussed in the present chapter we are concerned with the formation of positive ions at collisions between electrons and gas molecules. This phenomenon, known as ionization by collision, first becomes noticeable at energies slightly higher than those considered in the previous chapters, the appearance of positive ions in fact constituting an upper limit to the precise application of the diffusion methods.

When a stream of electrons passes through a gas, positive ions and additional electrons are produced by collisions, provided that the energies of some of the electrons exceed a critical value determined by the ionization potential of the gas. If the electrons flow between two electrodes, the current increases rapidly as the voltage is increased, until finally a spark passes. Townsend has shown that positive ions are produced first by collisions between electrons and gas molecules and then, as the sparking potential is approached, by collisions between positive ions and molecules.

Consider first the stage in which essentially all the ionization is produced by collisions between electrons and molecules. If  $n_0$  electrons are emitted from a plate and  $n$  arrive at a distance  $z$  from the plate, the number of electrons generated in a further distance  $dz$  is given by

$$dn = \beta n.dz,$$

where  $\beta$  is the average number of ions formed by an electron in moving 1 cm in the direction counter to the field. The quantity  $\beta$ , known as the ionization coefficient, may be taken as constant over the path when the pressure is sufficiently large for the electrons to attain a steady state after moving a small distance from the source. The number  $n$  is then given by

$$n = n_0 e^{\beta z}. \dots\dots\dots (64)$$

Experiments show that the ratio  $\beta/p$  depends only on the value of  $Z/p$ , a relationship which can be deduced from theoretical con-

siderations similar to those given in §1.4. In all cases,  $\beta/p$  increases with  $Z/p$  in the range  $Z/p < 10^3$ , being given approximately by an expression of the form\*

$$Ae^{-Bp/Z}.$$

At high values of  $Z/p$  the number of ions produced by collisions between ions and molecules becomes appreciable. Let  $\gamma$  denote the average number of electrons produced by a positive ion in moving 1 cm in the direction of the field. It can then be readily shown that if  $n_0$  electrons leave a plate the number arriving at a plane a distance  $d$  away is given by

$$n = n_0 \frac{(\beta - \gamma) \cdot \exp [(\beta - \gamma)d]}{\beta - \gamma \cdot \exp [(\beta - \gamma)d]}.$$

When  $\gamma = 0$ , this relation reduces to

$$n = n_0 e^{\beta d}.$$

It will be seen from the above equation that  $n$  becomes infinite when

$$\beta - \gamma \cdot \exp (\beta - \gamma)d = 0,$$

that is, when

$$d = \frac{\log \beta - \log \gamma}{\beta - \gamma}.$$

This relation allows the sparking distance to be calculated for given values of  $Z$  and  $p$ , and it has been found by Townsend and others that the calculated values agree closely with those determined experimentally.

## 6.2—The Motion of Electrons in a Gas under the Influence of Combined Electric and Magnetic Fields.

Before investigating the effect of electric waves on ionized gases, and in particular on the ionosphere, it is necessary to derive equations describing the motion of electrons in gases under the combined action of electric and magnetic fields. Such equations have been given by V. A. Bailey and L. G. H. Huxley.

\* Townsend, "Electricity in Gases," p. 294.

We begin by deriving a formula due to Bailey\*. The electric field considered is of a very general character, and is taken to be the resultant of any number of components having different amplitudes, directions, frequencies and damping; the magnetic field is taken as constant. The principal symbols are tabulated below:

$$\sigma = -e/m = 5.3 \times 10^{17} \text{ (e.s.u.)};$$

$$\tau = e^2/m = 2.54 \times 10^8;$$

$$H\mathbf{h} = \text{constant magnetic field vector, where } \mathbf{h} \text{ is a unit vector};$$

$$F = H\sigma/c, \mathbf{F} = F\mathbf{h};$$

$$E_n\mathbf{n} = \text{amplitude of a component of the electric field } \mathbf{E}, \\ \text{where } \mathbf{n} \text{ is a unit vector};$$

$$\mathbf{E} = \sum_n E_n \mathbf{n} T_n, \text{ where } T_n \text{ is a function of the time } t;$$

$$Z_n = E_n/\sqrt{2};$$

$$\omega_n = \text{angular frequency of } T_n;$$

$$\Phi_n = \text{phase angle of } T_n;$$

$$\nu_n = \text{damping coefficient of } T_n;$$

$$\mathbf{W} = \text{mean velocity of a group of electrons};$$

$$\nu = \text{collision frequency of an electron};$$

$$w = \text{mean work done on an electron per collision, at the time } t;$$

$$\bar{w} = \text{average value of } w \text{ taken over the longest period};$$

$$\partial = D + \nu, \text{ where } D = d/dt;$$

$$S = \frac{1}{\partial - iF}, \quad S' = \frac{1}{\partial + iF};$$

$$c_{mn} = \mathbf{m} \cdot \mathbf{n}, \quad s_{mn} = \mathbf{m} \times \mathbf{n}.$$

Using Townsend's definition of a collision between an electron and a molecule, the mean loss of momentum per second by an electron is  $\nu m \mathbf{W}$ . The equation of mean motion of an electron is therefore

$$\partial \mathbf{W} = -\sigma \mathbf{E} + \mathbf{F} \times \mathbf{W}. \quad \dots\dots\dots (65)$$

On multiplying this equation vectorially and scalarly by  $\mathbf{F}$  we obtain respectively

$$\partial(\mathbf{F} \times \mathbf{W}) = -\sigma \mathbf{F} \times \mathbf{E} - F^2 \mathbf{W} + (\mathbf{F} \cdot \mathbf{W}) \mathbf{F}$$

\* *Phil. Mag.*, 23, p. 774 (1937).

and

$$\partial(\mathbf{F}, \mathbf{W}) = -\sigma \mathbf{F} \cdot \mathbf{E},$$

from which it follows that

$$\partial^2(\mathbf{F} \times \mathbf{W}) = -\partial \sigma \mathbf{F} \times \mathbf{E} - \partial F^2 \mathbf{W} - \sigma (\mathbf{F} \cdot \mathbf{E}) \mathbf{F}.$$

Operating on (65) with  $\partial^2$ , and using this last result, we obtain

$$\partial^3 \mathbf{W} = -\partial^2 \sigma \mathbf{E} - \partial \sigma (\mathbf{F} \times \mathbf{E}) - \partial F^2 \mathbf{W} - \sigma (\mathbf{F} \cdot \mathbf{E}) \mathbf{F},$$

that is,

$$-\partial(\partial^2 + F^2) \mathbf{W} / \sigma = \partial^2 \mathbf{E} + \partial F \mathbf{h} \times \mathbf{E} + F^2 \mathbf{h}(\mathbf{h} \cdot \mathbf{E}). \quad \dots (66)$$

The particular integral of (66) is  $\mathbf{U}$ , where

$$-\mathbf{U} / \sigma = P \mathbf{E} + Q \mathbf{h} \times \mathbf{E} + R \mathbf{h}(\mathbf{h} \cdot \mathbf{E}), \quad \dots (67)$$

in which equation

$$\left. \begin{aligned} 2P &= \frac{2\partial}{\partial^2 + F^2} = S + S', \\ 2Q &= \frac{2F}{\partial^2 + F^2} = -i(S - S'), \\ 2R &= \frac{2F^2 \partial^{-1}}{\partial^2 + F^2} = \frac{2}{\nu + D} - 2P. \end{aligned} \right\} \dots (68)$$

The complementary function is  $\mathbf{V}$ , where

$$-\mathbf{V} / \sigma = e^{-\nu t} (\mathbf{a}_1 + \mathbf{a}_2 \cos Ft + \mathbf{a}_3 \sin Ft),$$

$\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$  being constant vectors such that  $\mathbf{V}$  satisfies (65) when  $\mathbf{E} = 0$ . This leads to the result

$$\mathbf{a}_1 = a \mathbf{h}, \mathbf{a}_2 = b \mathbf{h}_1, \mathbf{a}_3 = b \mathbf{h}_2,$$

where  $\mathbf{h}_1$  and  $\mathbf{h}_2$  are unit vectors perpendicular to  $\mathbf{h}$  and to each other, and  $a$  and  $b$  are arbitrary constants. Hence

$$-\mathbf{V} / \sigma = e^{-\nu t} (a \mathbf{h} + b \mathbf{h}_1 \cos Ft + b \mathbf{h}_2 \sin Ft). \quad \dots (69)$$

At the time  $t$  the mean work done per second on an electron is  $e \mathbf{E} \cdot \mathbf{W}$ , and in one second  $\nu$  collisions occur. Therefore

$$\nu w / \tau = -\mathbf{E} \cdot \mathbf{W} / \sigma = -\mathbf{E} \cdot \mathbf{U} / \sigma - \mathbf{E} \cdot \mathbf{V} / \sigma. \quad \dots (70)$$

From (67) it follows that

$$- \mathbf{E} \cdot \mathbf{U} / \sigma = \mathbf{E} \cdot (P\mathbf{E}) - \mathbf{h} \cdot (\mathbf{E} \times Q\mathbf{E}) + (\mathbf{h} \cdot \mathbf{E}) \cdot R(\mathbf{h} \cdot \mathbf{E}). \quad \dots (71)$$

Also,

$$\begin{aligned} \mathbf{E} \cdot (P\mathbf{E}) &= \sum_{m,n} E_m E_n (\mathbf{m} \cdot \mathbf{n}) T_m \cdot P T_n, \\ \mathbf{h} \cdot (\mathbf{E} \times Q\mathbf{E}) &= \sum_{m,n} E_m E_n \mathbf{h} \cdot (\mathbf{m} \times \mathbf{n}) T_m \cdot Q T_n, \\ (\mathbf{h} \cdot \mathbf{E}) R(\mathbf{h} \cdot \mathbf{E}) &= \sum_{m,n} E_m E_n (\mathbf{h} \cdot \mathbf{m}) (\mathbf{h} \cdot \mathbf{n}) T_m \cdot R T_n. \end{aligned}$$

Hence

$$- \mathbf{E} \cdot \mathbf{U} / \sigma = \sum_{m,n} E_m E_n T_m \cdot O_{mn} T_n, \quad \dots \dots \dots (72)$$

where

$$O_{mn} = (\mathbf{m} \cdot \mathbf{n}) P - \mathbf{h} \cdot (\mathbf{m} \times \mathbf{n}) Q + (\mathbf{h} \cdot \mathbf{m}) (\mathbf{h} \cdot \mathbf{n}) R.$$

It is simply shown that

$$\mathbf{m} \cdot \mathbf{n} = (\mathbf{h} \cdot \mathbf{m}) (\mathbf{h} \cdot \mathbf{n}) + (\mathbf{h} \times \mathbf{m}) \cdot (\mathbf{h} \times \mathbf{n}),$$

so that

$$O_{mn} = U_{mn} P - V_{mn} Q + W_{mn} \partial^{-1}, \quad \dots \dots \dots (73)$$

where

$$\left. \begin{aligned} U_{mn} &= (\mathbf{h} \times \mathbf{m}) \cdot (\mathbf{h} \times \mathbf{n}), \\ V_{mn} &= \mathbf{h} \cdot (\mathbf{m} \times \mathbf{n}), \\ W_{mn} &= (\mathbf{h} \cdot \mathbf{m}) (\mathbf{h} \cdot \mathbf{n}). \end{aligned} \right\} \quad \dots \dots \dots (74)$$

From equation (69) it also follows that

$$\begin{aligned} - \mathbf{E} \cdot \mathbf{V} / \sigma &= e^{-\nu t} \sum_n E_n T_n [a(\mathbf{h} \cdot \mathbf{n}) \\ &+ b(\mathbf{h}_1 \cdot \mathbf{n}) \cos Ft + b(\mathbf{h}_2 \cdot \mathbf{n}) \sin Ft]. \quad \dots \dots \dots (75) \end{aligned}$$

Thus

$$w\nu/\tau = \text{right-hand side of (72)} + \text{right-hand side of (75)}, \quad \dots \dots \dots (76)$$

and so

$$w = (\tau/\nu) \sum_{m,n} E_m E_n T_m \cdot O_{mn} T_n + w_0, \quad \dots \dots \dots (77)$$

where

$$w_0 = (\tau/\nu) \times \text{right-hand side of (75)}.$$

In general we may set

$$T_n = e^{-\nu_n t} \cos(\omega_n t + \Phi_n) = \mathcal{R}(e^{\alpha_n t + i\Phi_n}), \quad \dots (78)$$

where  $\mathcal{R}(y)$  denotes the real part of  $y$ ;  $\alpha_n = -\nu_n + i\omega_n$ , and  $\nu_n$ ,  $\omega_n$ ,  $\Phi_n$  are real.

As  $f(D)$  and  $\mathcal{R}$  are commutative operations on any function of  $t$ , it will be seen from the equations (68) and (73) that

$$2O_{mn}T_n = \mathcal{R}(2S_{mn}e^{\alpha_n t + i\Phi_n}),$$

where

$$\left. \begin{aligned} 2S_{mn} &= (U_{mn} + iV_{mn})S_n + (U_{mn} - iV_{mn})S'_n + 2W_{mn}\bar{\delta}_n^{-1}, \\ S_n &= \frac{1}{\mu_n + i\sigma_n}, S'_n = \frac{1}{\mu_n + i\sigma'_n}, \bar{\delta}_n^{-1} = \frac{1}{\mu_n + i\omega_n}, \\ \mu_n &= \nu - \nu_n, \sigma_n = \omega_n - F, \sigma'_n = \omega_n + F, \end{aligned} \right\} \dots (79)$$

that is,

$$2S_{mn} = A_{mn} + iB_{mn},$$

where

$$\left. \begin{aligned} A_{mn} &= |S_n|^2 (\mu_n U_{mn} + \sigma_n V_{mn}) + |S'_n|^2 (\mu_n U_{mn} - \sigma'_n V_{mn}) \\ &\quad + 2 |\bar{\delta}_n^{-1}|^2 \mu_n W_{mn}, \\ B_{mn} &= |S_n|^2 (\mu_n V_{mn} - \sigma_n U_{mn}) - |S'_n|^2 (\mu_n V_{mn} + \sigma'_n U_{mn}) \\ &\quad - 2 |\bar{\delta}_n^{-1}|^2 \omega_n W_{mn}. \end{aligned} \right\} (80)$$

We then have

$$\begin{aligned} T_m O_{mn} T_n &= \frac{1}{2} e^{-\nu_{mn} t} \cos(\omega_m t + \Phi_m) [A_{mn} \cos(\omega_n t + \Phi_n) \\ &\quad - B_{mn} \sin(\omega_n t + \Phi_n)] \\ &= \frac{1}{4} e^{-\nu'_{mn} t} [A_{mn} \{\cos(\omega'_{mn} t + \Phi'_{mn}) + \cos(\omega_{mn} t + \Phi_{mn})\} \\ &\quad - B_{mn} \{\sin(\omega'_{mn} t + \Phi'_{mn}) - \sin(\omega_{mn} t + \Phi_{mn})\}], \end{aligned}$$

where

$$\left. \begin{aligned} \omega_{mn} &= \omega_m - \omega_n, \omega'_{mn} = \omega_m + \omega_n, \\ \Phi_{mn} &= \Phi_m - \Phi_n, \Phi'_{mn} = \Phi_m + \Phi_n, \\ \nu'_{mn} &= \nu_m + \nu_n. \end{aligned} \right\} \dots (81)$$

Hence from (77) it follows that

$$w = \frac{\tau}{4\nu} \sum_{m,n} E_m E_n e^{-\nu'_{mn} t} [A_{mn} \{\cos(\omega_{mn} t + \Phi_{mn}) + \cos(\omega'_{mn} t + \Phi'_{mn})\} \\ + B_{mn} \{\sin(\omega_{mn} t + \Phi_{mn}) - \sin(\omega'_{mn} t + \Phi'_{mn})\}] \\ + w_0. \quad \dots\dots\dots (82)$$

Equation (82) is not exact, as the distribution of velocities has been neglected; further, the quantity  $\mathbf{W}$  in equation (65) corresponds to the momentum transfer, so that the identification of  $e\mathbf{E} \cdot \mathbf{W}$  with the mean work done per second on an electron is not quite accurate (see §3.1). If these corrections are taken into account a numerical factor is introduced not differing greatly from unity; and in the ionospheric calculations to be considered the resulting modification is unimportant.

When  $\mathbf{E}$  is a simple sinoidal field inclined at an angle  $\theta$  to  $\mathbf{F}$ , it follows from (82) that the average value of  $w$  taken over the cycle is

$$\bar{w} = \frac{\tau Z^2}{2} \left[ \frac{\sin^2 \theta}{\nu^2 + (F - \omega)^2} + \frac{\sin^2 \theta}{\nu^2 + (F + \omega)^2} + \frac{2 \cos^2 \theta}{\nu^2 + \omega^2} \right]. \quad (82a)$$

This simple case was considered earlier by V. A. Bailey and D. F. Martyn\*, who obtained the formula

$$\bar{w} = \frac{\tau Z^2}{2} \left[ \frac{1}{\nu^2 + (F_p - \omega)^2} + \frac{1}{\nu^2 + (F_p + \omega)^2} \right],$$

where  $F_p$  is the component of  $\mathbf{F}$  perpendicular to  $\mathbf{E}$ . Bailey later pointed out that an error has been made here by overlooking the effect of the component of  $\mathbf{F}$  parallel to  $\mathbf{E}$ . This case was investigated more fully by Huxley†, who took the velocity-distribution into account. His general formula for  $\bar{w}$  contains a term which is proportional to  $\cos^2 \theta$  and independent of  $F$ , corresponding to the third term in Bailey's formula. For the special case when  $\mathbf{E}$  is perpendicular to  $\mathbf{F}$ ,  $|(F \pm \omega)| \gg 1$ , and a Maxwellian distribution holds, his formula reduces to

$$\bar{w} = 1.22 \frac{\tau Z^2}{2} \left[ \frac{1}{(F - \omega)^2} + \frac{1}{(F + \omega)^2} \right].$$

\* *Phil. Mag.*, **18**, p. 369 (1934).

† *Phil. Mag.*, **23**, p. 442 (1937).

Equation (82) is adopted in the following sections of this chapter, and it is shown later in §6.4 that a special case of this equation can be derived in a very different manner.

### 6.3—The Effect of Thunderstorms on the Ionosphere.

A good deal of experimental evidence suggests that sporadic increases in the ionization density of the *E*-layer of the ionosphere are associated with the occurrence of thunderstorms in the lower atmosphere\*. As an illustration, we have the observations carried out in India by Bhar and Syam† at regular intervals over a long period; their observations may be analysed as shown in the following table, only those thunderstorms occurring within 200 km of the station being taken into account.

	Ionization normal	Ionization abnormal	Total
No thunderstorm	79 Days	22 Days	101 Days
Thunderstorm	1	20	21
Total	80	42	122

C. T. R. Wilson has proposed two theories to account for this correspondence¶. In the first it was suggested that the electrostatic field associated with a thundercloud, considered to be that of a vertical dipole, is sufficiently intense in the ionosphere to cause appreciable ionization. The second proposed that electrons present in the atmosphere between the earth and the thundercloud

\* Appleton and Naismith, *Proc.Roy.Soc.*, A, **137**, p. 36 (1932); Ranzi, "Nature," **130**, p. 368 (1932); Appleton, Naismith and Builder, "Nature," **132**, p. 340 (1933); Appleton and Naismith, *Proc.Phys.Soc.*, **45**, p. 389 (1933); Ratcliffe and White, *Proc.Phys.Soc.*, **45**, p. 399 (1933); Ratcliffe, *Sci. News Letter*, 15th Sept. (1934); Colwell, "Nature," **133**, p. 948 (1934); Ratcliffe and White, *Proc.Phys.Soc.*, **46**, p. 107 (1934).

† *Phil.Mag.*, **23**, p. 513 (1937).

¶ *Proc.Camb.Phil.Soc.*, **22**, p. 535 (1925); *Proc.Phys.Soc.*, **37**, p. 32D (1925); *Proc.Roy.Soc.*, A., **141**, p. 697 (1933).



are accelerated to very high velocities (as high as  $5 \times 10^9$  e. volts) and that some of these electrons reach the ionosphere, where they give rise to a marked increase in the ionization density.

A third explanation was suggested by Bailey and Martyn\* who proposed that the radiation field of a thunderstorm would increase the energy of free electrons in the ionosphere sufficiently to cause ionization by collision. Detailed calculations of the effect of the radiation field of a thunderstorm have been carried out by Healey†, and these calculations show that the observed effect can be accounted for in this manner. In the present section it is intended to give an outline of these calculations and a summary of the results obtained.

In order to calculate the increase in ionization density, it is necessary to determine the electron velocity  $u$  at each instant. From the principle of conservation of energy, it can be shown that the quantities  $w$  and  $u$  are related by the formula

$$\frac{1}{2} \lambda u^2 + u \dot{u} / \nu = w/m, \dots\dots\dots (83)$$

where  $\lambda$  denotes the mean proportion of its energy lost by an electron at a collision with a gas molecule, and  $\nu$  denotes the collision frequency. The quantities  $\lambda$  and  $\nu$  are functions of  $u$  which have been determined for air by Townsend and Tizard‡, some of their results are given in Table 23. Equation (83) may be solved by a graphical method such as that developed by Bailey and Somerville||, but in this case sufficiently accurate results are obtained by the method given previously in 1936¶; this method depends upon the fact that, when  $u$  is sufficiently large to cause appreciable ionization, the term  $u \dot{u} / \nu$  is small compared with the other two terms, so that

$$w/m \doteq \frac{1}{2} \lambda u^2. \dots\dots\dots (84)$$

The expressions on both sides are functions of  $u$ , the point of intersection of the curves  $(w/m, u)$  and  $(\frac{1}{2} \lambda u^2, u)$  determining the value of  $u$  at the particular instant.

Having obtained  $u$  as a function of  $t$ , the increase in ionization is derived by means of the equation

$$dN = \delta.N.dt,$$

\* *Phil.Mag.*, 18, p. 369 (1934).

† *Phil.Mag.*, 21, p. 187 (1936). *Analq.W'less.A'sia.Tech.Rev.*, 3, p. 215 (1938).

‡ *Proc.Roy.Soc., A*, 88, p. 336 (1913).

|| Bailey, *Phil.Mag.*, 23, p. 774 (1937).

¶ Healey, *loc. cit.*

where  $\delta = \beta W = p(\beta/p)W$ . It is more convenient to write this equation in the form

$$N = N_0 \exp \left( \int \delta dt \right). \dots\dots\dots (85)$$

The quantities  $W$  and  $\beta/p$  are also functions of  $u$  which may be obtained from the results given by Townsend and Tizard and by Sanders\* ; some of these values are given in Table 23.

Table 23.

$Z/p$	$u \times 10^7$ (cm/sec.)	$L \times 10^2$ (cm)	$\lambda \times 10^2$	$W \times 10^{-6}$ (cm/sec.)	$\beta/p$
0	1.1	3.3	0	—	—
2	5.4	3.28	0.26	1.8	$< 3 \times 10^{-5}$
6.4	7.3	2.92	0.63	3.6	$< 3 \times 10^{-5}$
10	7.8	2.82	1.13	5.2	$< 3 \times 10^{-5}$
30	9.5	2.73	3.4	12.4	$9 \times 10^{-4}$
50	11.6	2.78	5.5	17.3	$5.5 \times 10^{-2}$
100	14.5	2.72	8.6	27.0	$8 \times 10^{-1}$

(1) *The effect of a damped wave on the ionosphere.*

It has been shown that many atmospherics approximate to damped waves of very long wave-length†. Following Moullin†, the assumption is made that the radiation field of a thunderstorm may be represented approximately by the expression

$$E = \sqrt{2Z} e^{-kt} \cos \omega t,$$

where  $\omega = 2k$ , the energy being taken to be radiated at a single frequency.

For a damped wave, the coefficients  $A_{11}$  and  $B_{11}$  defined in §6.2 are given by the expressions

$$A = \frac{(\nu - k) \sin^2 \theta}{(\nu - k)^2 + (\omega - F)^2} + \frac{(\nu - k) \sin^2 \theta}{(\nu - k)^2 + (\omega + F)^2} + \frac{2(\nu - k) \sin^2 \theta}{(\nu - k)^2 + \omega^2},$$

\* F. H. Sanders, *Phys. Rev.*, **41**, p. 667 (1932).

† E. V. Appleton, R. A. Watson Watt and J. F. Herd, *Proc. Roy. Soc. A*, **111**, p. 615 (1926).

† E. B. Moullin, *J.I.E.E.*, **64**, p. 579 (1924).

$$B = -\frac{(\omega - F) \sin^2 \theta}{(\nu - k)^2 + (\omega - F)^2} - \frac{(\omega + F) \sin^2 \theta}{(\nu - k)^2 + (\omega + F)^2} - \frac{2\omega \cos^2 \theta}{(\nu - k)^2 + \omega^2},$$

where  $\theta$  is the angle between  $\mathbf{E}$  and  $\mathbf{F}$ .

The calculations are simplified if the mean value of  $w$  over a small period of time is used in equation (84). From (82) it is readily shown that, as  $w_0$  may be neglected, the average value of  $w$  between the times  $\psi_1/\omega$  and  $\psi_2/\omega$  is given by

$$\frac{1}{m} \times \bar{w}(\psi_1, \psi_2) = \frac{\sigma^2 Z^2 \omega}{2\nu(\psi_2 - \psi_1)} \left[ e^{-2kt} \left\{ \frac{A}{2k} - \frac{A \cos(2\omega t + \xi)}{2(\omega^2 + k^2)^{\frac{1}{2}}} \right. \right. \\ \left. \left. - \frac{B \sin(2\omega t + \xi)}{2(\omega^2 + k^2)^{\frac{1}{2}}} \right\} \right] \frac{\psi_1/\omega}{\psi_2/\omega},$$

where  $\xi = \tan^{-1}(\omega/k)$ . Usually it is sufficiently accurate to average over a quarter-period, but in certain cases more-accurate results have been obtained by splitting the first quarter-period into the two intervals  $(0, \pi/4)$ ,  $(\pi/4, \pi/2)$ .

The effect on the ionization density of variations in  $\nu_0$  (the collision frequency in the absence of the radiation field),  $\theta$  and  $Z$  will now be considered; the probable values of these quantities will be discussed later. In the calculations in sections (i) and (ii) we take  $\omega = 500\pi$  in accordance with Turner\*, and Appleton, Watson Watt and Herd. As a somewhat higher value has been suggested in a report of the Radio Research Board of Australia† we consider briefly in section (iii) the effect of taking  $\omega = 5000\pi$ . The quantity  $F$  occurring in the coefficients  $A$  and  $B$  is approximately  $10^7$  e.m.u.

Case 1— $\nu_0$ † varied;  $\theta = 0$ ,  $Z_1 = 1V/m$  and  $5V/m$ .

Using the method outlined above, the following values of  $u$  and  $\delta$ , corresponding to the calculated values of  $\bar{w}$ , were obtained for  $\nu_0 = 3 \times 10^4$  and  $Z = 1V/m$ .

\* L. B. Turner, "Wireless," 1931, p. 509.

† *Journal of the Council of Scientific and Industrial Research*, 10, No. 4, p. 133 (1937).

‡  $\nu_0 = 3 \times 10^4$  corresponds to  $p = 9 \times 10^{-5}$ , as  $\nu_0 = p\nu_0/L_0$ , the subscript  $0$  denoting the values of the various quantities in the absence of the radiation field.

Table 24

$$\theta = 0, Z = 1\text{V/m}, \nu_0 = 3 \times 10^4.$$

Interval†	Corresponding value of $u$ (cm/sec)	$\nu \times 10^{-4}$	$\delta$
$0 - \pi/4$	$16.8 \times 10^7$	54	$\div 6400$
$\pi/4 - \pi/2$	11.0	35	24
$\pi/2 - \pi$	10.3	33	5
$\pi - 3\pi/2$	9.0	28	—
$3\pi/2 - 2\pi$	7.7	23	—
† $\omega = 500\pi$ , so that the interval $(0, \pi/4)$ corresponds to 0.5 millisecc.			

From the values of  $\delta$  given in column 4, it follows that

$$\int \delta dt = \Sigma \delta \cdot \Delta t = 3.2 + 0.012 + 0.005$$

$$\div 3.2.$$

Then, from equation (85) it will be seen that the ionization density is increased by the factor  $N/N_0 \div e^{3.2} \div 25$

Similar calculations have been made for  $\nu_0 = 10^5$  and  $3 \times 10^5$  with  $Z = 1\text{V/m}$ , and for  $\nu_0 = 1.5 \times 10^5$ ,  $5 \times 10^5$  and  $1.5 \times 10^6$ , with  $Z = 5\text{V/m}$ . The results are summarized in Table 25.

Table 25

$$\theta = 0$$

$Z = 1\text{V/m.}$			$Z = 5\text{V/m.}$		
$\nu_0$	$p$	$N/N_0$	$\nu_0$	$p$	$N/N_0$
$3 \times 10^4$	$9 \times 10^{-5}$	$\sim 25$	$1.5 \times 10^5$	$4.5 \times 10^{-4}$	$> 10^3$
$10^5$	$3 \times 10^{-4}$	1.04	$5 \times 10^5$	$1.5 \times 10^{-3}$	1.25
$3 \times 10^5$	$9 \times 10^{-4}$	1.00	$1.5 \times 10^6$	$4.5 \times 10^{-3}$	1.00

Case 2— $Z$  varied ;  $\theta = 0$  ;  $\nu_0 = 3 \times 10^4$  and  $3 \times 10^5$ .

The values of  $N/N_0$  corresponding to various values of  $Z$  are shown in Table 26.

Table 26

$$\theta = 0$$

$\nu_0 = 3 \times 10^4$		$\nu_0 = 3 \times 10^5$	
$Z$	$N/N_0$	$Z$	$N/N_0$
2	$> 10^3$	—	—
1	$\sim 25$	10	$> 10^3$
0.75	3.5	7.5	$> 10^3$
0.5	1.25	5	10

Case 3— $\theta$  varied ;  $\nu_0 = 3 \times 10^4$  ;  $Z = 1V/m$ .

The effect of varying  $\theta$  is illustrated by Table 27, from which it will be seen that the maximum effect occurs at  $\theta = 0^\circ$  ; at  $\theta = 90^\circ$ , the increase in ionization is negligible.

Table 27

$$Z = 1V/m, \nu_0 = 3 \times 10^4.$$

$\theta$	$N/N_0$
$0^\circ$	$\sim 25$
$30^\circ$	9
$60^\circ$	1.3
$90^\circ$	1.0

(ii) *The effect on the ionosphere of a damped wave superposed on a constant electric field.*

The results given in the previous section are greatly modified if there exists a constant electric field in the ionosphere. Let the

two fields be

$$E_0 = \sqrt{2} Z_0$$

and

$$E_1 = \sqrt{2} Z_1 e^{-kt} \cos \omega t.$$

Then,

$$w/m = \frac{\sigma^2}{2\nu} [2Z_0^2 A_{00} + Z_1^2 e^{-2kt} \{A_{11} (\cos 2\omega t + 1) - B_{11} \sin 2\omega t\} \\ + 2Z_1 Z_0 e^{-kt} \{(A_{10} + A_{01}) \cos \omega t - B_{01} \sin \omega t\}].$$

The maximum effect occurs when the three vectors  $\mathbf{E}_1$ ,  $\mathbf{E}_0$  and  $\mathbf{F}$  are parallel; when  $\mathbf{F}$  is perpendicular to the electric fields, the effect is negligible. The first case will be considered in the following discussion.

The effect of varying  $Z_0$ ,  $Z_1$  and  $\nu_0^*$  will be considered.

Case 1— $Z_1$  varied; (a)  $Z_0 = 0.1$  V/m,  $\nu_0 = 2.7 \times 10^5$ .

(b)  $Z_0 = 0.5$  V/m,  $\nu_0 = 1.35 \times 10^6$ .

(a) This value of  $\nu_0$  corresponds to a pressure of  $8.7 \times 10^{-5}$  mm : for, at this pressure, and with  $E_0 = \sqrt{2} \times 10^{-3}$  V/cm,  $E_0/p = 16.3$ ; whence it follows from the results given by Townsend and Tizard that  $u_0 = 8.6 \times 10^7$  cm/sec,  $L_0 = 2.8 \times 10^{-2}$  cm and  $\nu_0 = pu_0/L_0 = 2.7 \times 10^5$ .

Using the method described above, and averaging  $w$  over quarter-periods of the damped wave  $E_1$ , the results given in Table 28 were obtained.

Table 28

$$\nu_0 = 2.7 \times 10^5, Z_0 = 0.1 \text{ V/m.}$$

$Z_1$ (V/m)	$N/N_0$
1.0	$\sim 100$
0.75	4
0.5	2

(b) The calculated results are given in Table 29.

\*  $\nu_0$  denotes the value of the collision frequency in the absence of the radiation field  $Z_1$ , i.e., when the steady field  $Z_0$  alone is present.

Table 29

$$\nu_0 = 1.35 \times 10^6, Z_0 = 0.5 \text{ V/m.}$$

$Z_1$ (V/m)	$N/N_0$
5.0	$> 10^3$
3.75	$\sim 10^3$
2.5	$\sim 30$

Case 2— $\nu_0$  varied ; (a)  $Z_1 = 0.5 \text{ V/m}$ ,  $Z_0 = 0.05 \text{ V/m}$ .

(b)  $Z_1 = 5.0 \text{ V/m}$ ,  $Z_0 = 0.5 \text{ V/m}$ .

The manner in which the effect depends upon  $\nu_0$  (and hence upon the pressure) for given values of  $Z_1$  and  $Z_0$  is illustrated by the results given in Table 30.

Table 30

(a) $Z_1 = 0.5 \text{ V/m}$ , $Z_0 = 0.05 \text{ V/m}$		(b) $Z_1 = 5.0 \text{ V/m}$ , $Z_0 = 0.5 \text{ V/m}$	
$\nu_0$	$N/N_0$	$\nu_0$	$N/N_0$
$10^5$	$\sim 100$	$10^6$	$> 10^3$
$2.0 \times 10^5$	2	$2.0 \times 10^6$	$\sim 10^3$
$2.3 \times 10^5$	1.3	$2.3 \times 10^6$	13
$3.5 \times 10^5$	1.00	$3.5 \times 10^6$	1.00

Case 3— $Z_0$  varied ; (a)  $Z_1 = 0.6 \text{ V/m}$ ,  $\nu_0 = 1.5 \times 10^5$ .

(b)  $Z_1 = 6.0 \text{ V/m}$ ,  $\nu_0 = 1.5 \times 10^6$ .

The variation of the ionization density with  $Z_0$ , for a fixed value of  $\nu_0$ , is shown in Table 31.

Table 31

(a) $Z_1 = 0.6 \text{ V/m}, \nu_0 = 1.5 \times 10^5$		(b) $Z_1 = 6 \text{ V/m}, \nu_0 = 1.5 \times 10^6$	
$Z_0 \text{ (V/m)}$	$N/N_0$	$Z_0 \text{ (V/m)}$	$N/N_0$
0.012	1.5	0.12	$\sim 50$
0.05	$\sim 20$	0.5	$> 10^3$
0.10	$\sim 100$	1.0	$> 10^3$

(iii) *The effect of a radiation field different from that considered in sections (ii) and (iii).*

The numerical results given in the tables above are not greatly affected if somewhat different expressions are taken for the radiation field of the thunderstorm; this is the case if the field is represented by a pulse lasting one millisecond or by an expression of the form

$$E = \sqrt{2} Z e^{-kt},$$

assuming the amplitudes to be of the same magnitude as before. The reason is that, for the values of  $\nu_0$  and  $Z$  considered, the increase in ionization depends upon the amount by which  $Z$  exceeds a critical value, and the period for which it exceeds this value. It follows from this fact that the ionization produced by a damped wave decreases as the frequency of the wave is increased. Tables 32 and 33 show the effects produced by waves of frequencies  $500\pi$  and  $5000\pi$  in two cases typical of those considered in sections (i) and (ii).

Table 32

$$Z_0 = 0, \nu_0 = 3 \times 10^5, \theta = 0.$$

	$\omega = 500\pi$	$\omega = 5000\pi$
$Z_1 \text{ (V/m)}$	$N/N_0$	$N/N_0$
10	$> 10^3$	$\sim 25$
7.5	$> 10^3$	3.5
5	10	1.25



Table 33

$$Z_1 = 6 \text{ V/m}, \nu_0 = 1.5 \times 10^6, \theta = 0.$$

	$\omega = 500\pi$	$\omega = 5000\pi$
$Z_0 \text{ (V/m)}$	$N/N_0$	$N/N_0$
0.12	$\sim 50$	1.5
0.5	$> 10^3$	$\sim 20$
1.0	$> 10^3$	$\sim 100$

An estimate of the approximate amplitude of the radiation field can be made from the data given by Appleton, Watson Watt and Herd. They consider that the electric moment of an average lightning flash is about  $2 \times 10^{17}$  e.s.u., and deduce that the field strength at a distance of 3000 km. from the source is approximately 0.06 V/m. From this value of the electric moment, it can be shown that the maximum field strength at the ionosphere is not less than 1.5 V/m; alternatively, using the value 0.06 V/m for the field strength at a distance of 3000 km, and applying Watson's formula, the value 1 V/m is obtained for the field intensity at the ionosphere. Further, in the report of the Australian Radio Research Board, the mean peak power radiated by a thunderstorm was estimated to be  $1.5 \times 10^9$  watts; this value corresponds to a maximum field strength of about 2.3 V/m at the E-layer. The agreement between these estimates is seen to be very satisfactory; we may therefore regard 2 V/m as the maximum value of  $Z$  produced by an average thunderstorm. The value given by Bailey and Martyn, namely 0.6 V/m, appears to be somewhat low; and as the increase in ionization density increases more rapidly than  $Z^2$ , an error of this magnitude would lead to a considerable modification of the conclusions.

Observations made by Munro and Huxley\* show that about 7 per cent. of thunderstorms have an intensity 2.5 times the average, and something like 1 per cent. an intensity 5 times the average. This shows that field strengths of 5 V/m at the ionosphere are not

\* G. H. Munro and L. G. H. Huxley, Report of the Australian Radio Research Board, No. 5, p. 9 (1932).

uncommon, and that, occasionally, values as high as 10 V/m may occur.

From the tables, it is clear that the maximum effect occurs when  $\theta$  is small. If the thunderstorm be regarded as a vertical dipole, the maximum value of  $Z$  in the ionosphere will be that due to radiation inclined at  $45^\circ$  to the horizontal. Thus, the effect on the upper atmosphere of a thunderstorm of given intensity will be greatest in those regions where the magnetic dip lies between  $30^\circ$  and  $60^\circ$ .

It is apparent from the calculations made above that the radiation field from a lightning flash must produce a notable increase in the ionization density of the E-region in the ionosphere, provided that radiation of suitable intensity penetrates to a region in which the collision frequency is sufficiently small. Thus, an appreciable effect occurs for all values of  $\nu_0$  less than  $10^6$  if the radiation field  $Z$  has a value of at least 5 V/m, as shown in Table 25. For those occasional flashes in which  $Z$  may approach 10 V/m, there must be marked increases in the ionization density, even in a region in which  $\nu_0$  is as high as  $2 \times 10^6$ . Now it has already been shown that radiation fields of 5 V/m may frequently be produced, so that it only remains to investigate the possibility of penetration to regions in which  $\nu_0$  has a value less than  $10^6$ .

It may first be noted that Green and Builder\* have inferred, from long-wave polarisation measurements made by Hollingworth†, that continuous-wave signals having frequencies of about 20 kc penetrate at night to regions in which the collision frequency has a value much less than  $7 \times 10^6$ . A closer approximation to the appropriate value of  $\nu_0$  may, however, be obtained by considering the available measurements of reflection heights of long-wave signals in conjunction with the following table relating  $\nu_0$  to height. Assuming that the collision frequency at 90 km is  $10^6$ ‡ and using a scale height factor of 9 km§ it follows that the variation of  $\nu_0$  with height is :—

Height (km) :	75	80	85	90	95	100	105.
$\nu_0 \times 10^{-6}$ :	5.3	3.0	1.7	1.0	0.57	0.33	0.19.

\* A. L. Green and G. Builder, *Proc.Roy.Soc., A.*, **145**, p. 145 (1934).

† J. Hollingworth, *Proc.Roy.Soc., A.*, **119**, p. 444 (1928).

‡ See Martyn, *Proc.Phys.Soc.*, **47**, p. 323 (1935).

§ See J. E. Best and J. A. Ratcliffe, *Proc.Phys.Soc.*, **50**, p. 233 (1938).

Unfortunately, the number of observations on reflection heights at long wavelengths is small; and, due to the relatively greater technical difficulties of the experimental procedure at the lower frequencies, the results are liable to uncertainties. For example, in some early experiments with long waves\*, it was found that the height of reflection rose only from 74 km during the day to 76 km at night. The later experiments made by Hollingworth in 1928 do not confirm the first results; more recent experiments performed by Best, Ratcliffe and Wilkes† indicate a much greater range of heights. Although the last-mentioned observations are liable to some uncertainty, due to the difficulty of ascertaining the order of the interference fringes, it is possible to infer that the reflection heights are either 74 km during the day and 92 km at night or, alternatively, 85 and 102 km respectively. Even in these observations, however, measurements were made only on a few occasions during a total period of time not exceeding a few months.

Finally, it is of interest to notice that observations on multiple reflections of atmospherics between the earth and the ionosphere have been reported by Laby, Nicholls, Nickson and Webster‡, the estimated reflection heights lying between 78 and 82 km.

The available evidence therefore suggests that the height of reflection at long wave lengths during the day is not likely to be much less than 75 km nor much greater than 85 km, the corresponding values of  $\nu_0$  being  $5.3 \times 10^6$  and  $1.7 \times 10^6$ . It follows that in the absence of any additional electric field, only the relatively rare lightning flashes having radiation fields of about 10 V/m will produce marked changes in the ionization density in the reflecting region. At night, however, when the height of reflection may exceed 90 km and possibly 100 km, the corresponding values of  $\nu_0$  indicate that a notable increase in the ionization will be caused by any lightning flash which produces a radiation field greater than about 2 V/m. If, however, there always exists in the ionosphere a small, constant electric field‡, and if it is supposed that this field is of the order 0.5 V/m, it follows from the tables in section (ii) that the radiation field from a thunderstorm will often

\* Hollingworth, *J.I.E.E.*, **64**, p. 579 (1926).

† *Proc.Roy.Soc., A.*, **156**, p. 614 (1936).

‡ "Nature," **139**, p. 837 (1937); see also Laby, McNeill, Nicholls and Nickson, *Proc.Roy.Soc., A.*, **174**, p. 145 (1940).

§ See W. Kolhorster, "Nature," **132**, p. 407 (1933); and Huxley, "Nature," **134**, p. 571 (1934).

cause a marked increase in the ionization density, even during the day.

It is now possible to make some observations of a general nature concerning the effect of a thunderstorm on the propagation of radio waves in the ionosphere. In the first place, as the attenuation of a wave passing through an ionized medium depends upon both  $\nu$  and  $N$ , it follows that a temporary increase in  $\nu$  produces a short-period modulation of the wave. The corresponding increase in  $N$  is effective over much longer periods, as the rate at which  $N$  returns to its original value depends upon the coefficients of recombination and attachment. It may therefore be expected that, for those waves which are reflected at a region above the portions of the layer in which the thunderstorm produces an increase in ionization, the observed effect will be a reduction in the amplitude of the signal received. In other cases, however, in which the frequency is such that the wave is reflected from that region in which  $N$  has been notably increased by the radiation field, the observed effect will be an increase in the intensity of the signal received. Further, an increase in ionization may cause waves of certain frequencies to be reflected from a lower height than usual.

#### 6.4—Production of Artificial Auroræ.

It has already been shown in §6.3 that the radiation field of an intense lightning discharge can cause an appreciable increase in the ionization density of the lower strata of the ionosphere. Equation (82a) suggests further that if the angular frequency  $\omega$  of an electric wave is approximately equal to  $F$ ,  $\omega$  can be very large even for relatively low values of  $Z$ ; so that ionization by collision may be produced by a radio wave having an angular frequency approximately equal to the local gyro-frequency. Bailey has calculated the minimum power required for a gyro-wave to produce a visible glow in the upper atmosphere\*; an outline of his method is given in the present section.

The calculations in §§6.2 and 6.3 involve values of the electric field actually within the ionosphere. Here, on the other hand, we consider the effect of an electric wave on the ionosphere, taking

\* *Phil. Mag.*, **23**, p. 929 (1937); **26**, p. 425 (1938).

into account the decrease in the field strength due to absorption along its path through the layer.

(i) *The mean work done on an electron in the ionosphere by an elliptically polarized wave of frequency close to the gyro-frequency.*

**E, H** = electric and magnetic vectors of the wave, in e.s.u. and e.m.u. respectively ;

$N$  = electron density ;

$p_0^2 = 4\pi N\tau$  ( $= 3.19 \times 10^9 N$ ) ;

$\omega_0 = p_0^2/\omega$  ;

$\mu$  = refractive index ;

$\kappa$  = coefficient of absorption ;

$cq = \mu - i\chi$ , where  $\chi = \kappa c/\omega$  ,

$\Phi$  = angle between direction of propagation of the wave and the earth's magnetic field ;

**A** = vector potential of the wave.

The  $x$ -axis is chosen to lie along the direction of propagation of the wave, so that we may write

$$\mathbf{A} = \mathcal{A}e^{i\omega(t - qx)},$$

it being understood that in this relation we are concerned only with the real part. The other axes are chosen so that **F** lies in the  $xz$  plane.

Let  $U$  denote the quantity of radiant energy passing per second across unit surface placed normal to the  $x$ -axis, and let **P** denote Poynting's vector. Then,

$$U = \mathbf{i} \cdot \mathbf{P},$$

where **i** is a unit vector parallel to the  $x$ -axis and  $\mathbf{P} = (c/4\pi) \mathbf{E} \times \mathbf{H}$  ; so that, taking mean values, it can be shown that  $\bar{U}$  can be expressed in either of the two equivalent forms :

$$\bar{U} = \frac{\omega^2 \mu}{8\pi c} |\mathcal{A}|^2 e^{-2\kappa x}, \quad \dots \dots \dots (86)$$

and

$$\bar{U} = \frac{c}{8\pi} \cdot \frac{\mu}{\mu^2 + \chi^2} |H_y|^2 (1 + |R|^2),$$

where  $R$  (the polarization number) equals  $H_z/H_y$  ; the moduli of  $\mathcal{A}$ ,  $H$  and  $R$  are taken as these quantities may be complex.

In passing through a cylindrical volume of length  $dx$  and unit cross-section, the wave expends energy on the  $Ndx$  electrons contained therein at the rate  $U(x) - U(x + dx)$ , that is, at the rate  $-(\partial U/\partial x)dx$ . Hence the mean energy expended on one electron per collision is given by

$$\bar{w} = -\frac{1}{N\nu} \cdot \frac{\partial \bar{U}}{\partial x}.$$

As the mean value is taken over the time alone, it follows from equation (86) that

$$\frac{\partial \bar{U}}{\partial x} = -2\kappa \bar{U}, \quad *$$

so that we have

$$\bar{w} = 2\kappa \bar{U}/(N\nu). \quad \dots\dots\dots (87)$$

Bailey has given an alternative proof of this equation.

We now consider the effect of a plane wave whose angular frequency  $\omega$  equals  $(1 + \varepsilon)F$ , where  $\varepsilon$  is small compared with unity. As there is no appreciable resonance effect for the ordinary component, we need consider only the extraordinary component when the wave enters the ionosphere. We may therefore set  $\bar{U}$  equal to  $\bar{U}_e u_s$ , where  $\bar{U}_e$  is the mean energy-flux density at the boundary of the ionosphere due to the extraordinary component alone, and

$$\log u_s = -2 \int_0^s \kappa ds,$$

$s$  being the distance traversed by this component in the layer.

It can be shown† that

$$\bar{U}_e/\bar{U}_p = \Psi \mu_e/(\mu_e^2 + \chi_e^2),$$

where

$$\Psi = \frac{|R_p - R_0|^2}{|R_e - R_0|^2} \cdot \frac{1 + |R_e|^2}{1 + R_p^2}$$

and the subscripts  $p$ ,  $o$  and  $e$  refer respectively to the original plane

\*For a heterogeneous medium this formula still holds true.

† Bailey (1937).

wave and its elliptically polarized ordinary and extraordinary components.

For the extraordinary wave, therefore, equation (87) becomes

$$\bar{w}_e = \tau Z^2 \Psi a_s \Gamma,$$

where

$$\Gamma = \frac{2\mu_e \chi_e}{v\omega_0(\mu_e^2 + \chi_e^2)}.$$

If we limit ourselves to the case in which  $\omega_0^2 \ll v^2$ , the expression for  $\bar{w}_e$  reduces to\*

$$\bar{w}_e = \tau Z^2 a_s \left( \frac{\frac{1}{2} \sin^2 \theta}{v^2 + (\omega - F)^2 - v^2 p'_e} \right), \quad \dots \dots (88)$$

where  $\theta$  is the angle between the electric vector  $\mathbf{E}$  of the original wave and the vector  $\mathbf{F}$ , and

$$p' = \frac{\tan^2 \Phi + 2 \cot^2 \theta}{\tan^2 \Phi + 2} - \frac{p_0^2 (1 + \cos^2 \Phi)}{2v^2}.$$

When the electron density  $N$  is small, we have  $a_s \doteq 1$  and  $|p'_e| \ll 1$ , so that the above expression for  $\bar{w}_e$  is then in close agreement with that which would be obtained for this special case by substitution in equation (82a) in §6.2. As (82a) was derived without reference to the fundamental equations of Maxwell and Lorentz or to Poynting's theorem, on which the above formula for  $\bar{w}_e$  is ultimately based, we may take this agreement to constitute a valuable check on the calculations.

In the more general case it is necessary to calculate the value of  $a_s$ . For example\*, assuming the earth's magnetic field to be vertical and that  $N < 800$ , and denoting the angle of incidence on the layer by  $i_0$ , we have

$$\Phi = i_0 \text{ and } s = y \sec i_0,$$

where  $y$  is the height of the point above the lower boundary of the layer. The quantity  $a_s$  is then given by

$$\log a_s = -0.0532 (\cos i_0 + \sec i_0) I,$$

\* Bailey (1938).

where

$$I = \int_0^y \frac{N\nu}{\nu^2 + \varepsilon^2 F^2} dy.$$

Assuming that

$$\nu = \nu_0 e^{-n y},$$

where  $\nu_0 = 1.1 \times 10^6$  and  $n = 10^{-6}$ , and assuming Martyn's distribution of electronic concentration,

$$N = f(\nu) = \nu^{-1.0},$$

the above integral becomes

$$-nI = \int_{\nu_0}^{\nu} \frac{f(\nu).d\nu}{\nu^2 + \varepsilon^2 F^2}.$$

We are thus able to compute  $a_s$ , and hence  $\bar{w}_e$ .

In this way the values of  $\bar{w}_e$  resulting from a wave with an angle of incidence  $i_0$  equal to  $45^\circ$  have been computed for different values of  $\omega$  in the neighbourhood of  $8 \times 10^6$  (the value of  $F$  corresponding to London). From these, the values of the quantity  $N\nu\bar{w}_e$  at each of four different levels in the  $E$ -region have been determined,

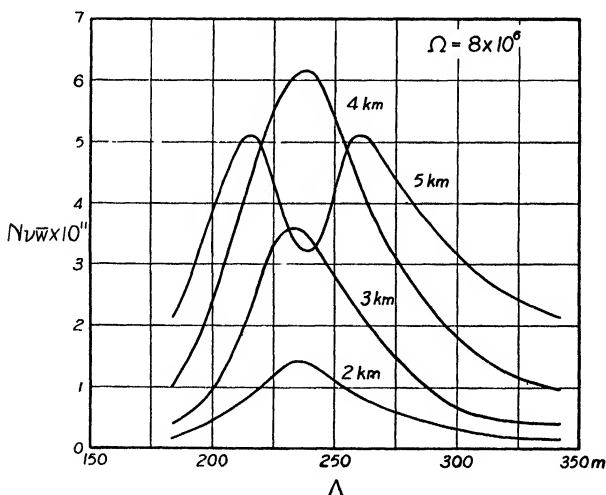


FIG. 39. Effect at various levels in the ionosphere of the extraordinary component, as a function of the wave-length.



and are given in terms of the wave-lengths by means of the curves in figure 39.

(ii) *Power required to produce a discharge.*

As the intensity of a gyro-wave is increased, the primary effect is to increase the velocities of agitation, so that eventually collisions occur which cause the molecules to emit light, or fresh electrons, or both.

It is therefore of interest to determine the minimum power  $P_m$  which may need to be radiated from an appropriate system of aerials in order to maintain a steady electrical discharge in the  $E$ -layer at night.

We first consider an aerial system consisting of a horizontal half-wave Hertzian oscillator placed at a height  $\lambda/4$  above a highly reflecting ground, where  $\lambda$  denotes the wave-length, and for simplicity again take the terrestrial magnetic field to be vertical.

If the radiated power be  $P$  kilowatts, the r.m.s. electric intensity  $Z$  at the lower part of the  $E$ -layer vertically above the oscillator is given by the formula\*

$$Z^2 = 5.8 \times 10^{-9} P$$

when  $Z$  is expressed in volts per centimetre.

As the vertically radiated wave is plane, it may be analysed into two circularly polarized components of equal intensities, one of which imparts only relatively negligible energy to the electrons; thus the effect on the electrons may be attributed entirely to the extraordinary circular wave, which has a rotating constant vector of magnitude equal to  $\frac{1}{2}(\sqrt{2}Z)$ , that is, to  $Z/\sqrt{2}$ .

The waste of power in the radiation of an ordinary component can be avoided by adding to the Hertzian oscillator an orthogonal one, and radiating the power  $\frac{1}{2}P$  from each. In this way a vertical, circularly polarized gyro-beam with rotating constant vector of magnitude  $E$  (equal to  $Z$ ) may be produced by means of an aerial system radiating the power  $P$  kilowatts, where

$$E^2 = 5.8 \times 10^{-9} P, \quad \dots\dots\dots(89)$$

$E$  being expressed in volts per centimetre.

\* See A. L. Green, *Amalg. W'less. A'sia. Tech. Rev.*, 3, p. 130 (1938). The lower part of the  $E$  layer is taken to be 90 km high.

It can be shown\* that at a given pressure  $p$  a rotating constant force  $E$  yields the same value of  $u$  as an equal steady force  $X$  or a stationary alternating force of equal r.m.s. value  $Z$ .

The experiments of H. A. Wilson† and D. M. Myers‡ show that electric discharges can occur in tubes containing air when  $X/p$  or  $Z/p$  in the uniform column is as low as 16 approximately. We may therefore conclude that two of the necessary conditions for producing a glow discharge, namely the generation of fresh electrons and light, are satisfied when

$$E/p \geq 16,$$

that is, when

$$P \geq 4.4 \times 10^{10} p^2. \quad \dots \dots \dots (90)$$

Bailey has computed the values of  $\bar{w}_e$  for a wave having an angular frequency exactly equal to the gyro-frequency. The results are tabulated below.

Table 34

$$i = 45^\circ, Z = 5 \text{ mV/m}, P \approx 10 \text{ kW}, \epsilon = 0$$

$y \text{ (km)}$	0	1.5	2.7	4.0	4.5	5.0	5.5	6.0
$a_s$	1	0.96	0.84	0.47	0.27	0.103	0.020	0.001
$\bar{w}_e \times 10^{18}$	2.2	2.8	3.2	2.3	1.5	0.6	0.13	0.01
$N$	1	4.5	14.9	54.6	90	150	244	400
$\nu \times 10^{-5}$	11	9.5	8.4	7.4	7.0	6.6	6.3	6.0

As shown in this table, the maximum effects caused by a low-powered gyro-wave occur at that level in the  $E$ -layer which corresponds to  $y = 2.7 \text{ km}$ ,  $\nu = 8.4 \times 10^3$ ,  $a_s = 0.84$ , and  $N = 15$ . It is easy to deduce that at that level, with an assumed temperature of about  $15^\circ\text{C}$ ., the gas pressure  $p$  is approximately  $2 \times 10^{-3} \text{ mm}$  of mercury.

We then conclude from (90) that both visible light and fresh electrons are generated at collisions when the power radiated from

\* Bailey (1938).

† *Proc.Camb.Phil.Soc.*, 11, pp. 249 and 391 (1902).

‡ Unpublished experiments with high-frequency discharges made in Sydney on the lines developed by Townsend and his associates.

our simple polarizing aerial system is not less than  $P_m$ , where

$$P_m = 2 \times 10^5 \text{ kW.}$$

The supply of electrons needed for initiating and maintaining this glow discharge is provided by those natural processes which are normally responsible for maintaining throughout the night the considerable concentrations of electrons known to exist in the *E*-layer. Alternatively, the generation of electrons by collisions under the influence of the above gyro-wave will also serve to maintain the discharge (see Bailey, 1938).

The minimum power required can be reduced considerably by using two orthogonal arrays of Hertzian oscillators. If each array consists of  $n$  adjacent, parallel rows, each containing  $n$  parallel, half-wave oscillators spaced at a distance  $\lambda/2$  apart, the minimum power required is

$$P_m = 2 \times 10^5/n^2 \text{ kW.}$$

Thus, with a system of 4050 half-wave aeriels, and the angular frequency of the oscillation equal to the local gyro-frequency, it would appear possible to generate an observable celestial glow at night with a power as low as 100 kW.

### 6.5—The Interaction of Radio Waves in the Ionosphere.

The cross-modulation between transmitting stations, known as the "Luxemburg effect," was first observed some years ago in Holland and England between the transmitters at Beromünster (653 kc) and Luxemburg (252 kc)\*, and later between other European stations. During the reception from Beromünster and a number of other medium-wave stations, the modulation of the long-wave transmitter at Luxemburg could also be heard, this interference being especially distinct during the pauses in the programme. It was clear that poor selectivity of the receivers concerned and the intrusion of harmonics generated by the station at Luxemburg could not be responsible for this effect. The fact that the interference was observed only during the night, that is, when there are strong sky-waves, indicated that the interaction occurred in the ionosphere.

\* See Tellegen, "Nature," **131**, p. 840 (1933).

Bailey and Martyn\* explained this phenomenon by taking into account the effect of the radiation field of a transmitter on the energy of the free electrons in the ionosphere. Any change in the velocity of agitation will cause a corresponding change in  $\nu$ , and hence a change in the absorption coefficient. If the transmitted wave is modulated at a certain frequency, the absorbing power of that part of the ionosphere in the vicinity of the station will vary at the same frequency, so that this modulation will be impressed in part on any other carrier-wave which may traverse this region.

Their calculations led to a number of important conclusions :

(a) Interaction is most marked when the first transmitter is of high power and fairly long wave-length, and when the second wave is reflected from a region of the layer in the neighbourhood of the first station, the optimum effect occurring when  $\omega_1^2 \cos^2 i_1 = \omega_2^2 \cos^2 i_2$ , where  $i$  is the angle of incidence on the ionosphere and the subscripts 1 and 2 refer to the first and second waves respectively.

(b) The impressed modulation is proportional to the power of the first transmitter.

(c) The impressed modulation is inversely proportional to  $\sqrt{(f^2 + 780^2)}$ , where  $f$  is the modulation frequency of the first wave ; so that there is an inherent distortion of the impressed modulation in the range of higher audible frequencies.

These predictions were found to be in good agreement with later experimental results†.

Bailey's revised calculations of the effect of electric waves on the ionosphere led to two additional conclusions‡ :

(a) Low-power stations whose angular frequency is close to the local gyro-frequency can cause observable interaction with a second station. Thus, a transmitter radiating at the rate of only one or two kilowatts and whose angular frequency is within about 5 per cent. of the gyro-frequency might be expected to produce appreciable interaction with long and medium waves.

(b) Two waves whose frequencies differ by an audible frequency may cause an audible modulation of a third wave whose frequency differs considerably from those of the other two.

\* *Phil. Mag.*, **18**, p. 369 (1934).

† Bailey and Martyn, "Nature," **135**, p. 585 (1935); and J. Grosskopf, *Hochfrequenztechn.u. Elektroak.*, **51**, p. 18 (1938).

‡ *Phil. Mag.*, **23**, p. 929 (1937).

The first of these predictions has been completely verified\*. Observations carried out by W. L. Hakefost† lend some support to the second, although experimental confirmation is difficult to obtain.

We now give a brief outline of Bailey's later calculations relating to interaction phenomena.

(i) *The modulation impressed by a long-wave station on the wave from a second station.*

In general,  $\nu \ll F$ ; and for a long-wave station  $\omega \ll F$ . Also, it may be assumed as a first approximation that the electric field in the part of the  $E$ -layer under consideration is the same as the field produced by the emitted plane wave at points just below the layer. We may therefore adopt equation (82a) in §6.2 as the formula for  $\bar{w}$  corresponding to such a wave.

For most parts of the  $E$ -layer which are notably subjected to the emission from a typical aerial system, the values of  $\sin^2\theta$  and  $\cos^2\theta$  are of the same order; we may therefore, without serious error, assign to each quantity a value equal to the mean value  $\frac{1}{2}$ .

In this case, then, we obtain from equation (82a) the following approximate formula

$$\bar{w} = \frac{\frac{1}{2}\tau Z^2}{\nu^2 + \omega^2} \quad \dots\dots\dots(91)$$

To determine the temporal variation  $\Delta\nu$  of the collision frequency  $\nu$  we proceed as follows.

The relationship between  $\nu$  and  $\bar{w}$  is given by equation (83) in §6.3, which may be written in the form

$$aD\nu + \eta = \bar{w}, \quad \dots\dots\dots(83)$$

where  $a = ml^2$  and  $\eta$  denotes the mean energy lost by an electron at a collision. Denoting the corresponding values of these quantities in the steady state by the subscript zero, it follows from this equation that

$$\eta_0 = \bar{w}_0.$$

If the temporal variation  $\Delta\bar{w}$  of  $\bar{w}$  about the equilibrium value  $\bar{w}_0$  be small, it follows from (83) that

$$\frac{d}{dt} \Delta\nu + R. \Delta\nu = a^{-1} \Delta\bar{w}, \quad \dots\dots\dots(92)$$

\* Bailey, "Nature," 139, p. 838 (1937).

† "Wireless Engineer," 13, p. 298 (1936).

where  $R = a^{-1} d\eta_0/d\nu_0$ , the subscript 0 denoting the equilibrium values.

If the wave is modulated at an audio frequency  $n/2\pi$  we have

$$Z = Z_0 (1 + M \sin nt), \text{ where } M < 1;$$

so that

$$\bar{w} = 2M\bar{w}_0 \sin nt - \frac{1}{2}M^2\bar{w}_0 \cos nt + \frac{1}{2}M^2\bar{w}_0.$$

It then follows from the differential equation (92) that the permanent part of  $\nu$  is given approximately by the formula

$$\nu = \frac{2M\bar{w}_0}{a(R^2 + n^2)^{\frac{1}{2}}} \sin (nt - \Phi),$$

where

$$\tan \Phi = n/R.$$

Thus  $\nu$  is modulated at the frequency  $n/2\pi$  and with a coefficient of modulation  $M'$  given by

$$M' = 2M\bar{w}_0\delta/aR\nu_0, \quad \dots \dots \dots (93)$$

where

$$\delta = \frac{1}{\sqrt{(1 + n^2/R^2)}}. \quad \dots \dots \dots (94)$$

Consider now a second wave traversing the region under discussion. If  $E_0$  denotes the intensity on striking the ionosphere and  $E_1$  the intensity of the emergent wave, it can be shown\* that

$$E_1 = E_0 \cdot \exp (-C_0\nu),$$

where  $C_0$  is a quantity depending on the frequency of the wave, the length of path, and the density and gradient of ionization in the layer. Remembering that  $\nu$  is modulated by the first wave to a degree expressed by equation (93), it will be seen that

$$E_1 = E_0 \cdot \exp [-C_0\nu_0 \{1 + M' \sin (nt - \Phi)\}].$$

From this result it follows that the amplitude of the emergent wave is modulated at the angular frequency  $n$ ; and as  $C_0\nu_0$  is of the order unity, the degree of modulation imposed on the second wave is given approximately by

$$M'' = C_0\nu_0 M'. \quad \dots \dots \dots (95)$$

\* See Bailey and Martyn, *Phil. Mag.*, 18, p. 369 (1934).

Assuming for simplicity that the collisions involve a constant coefficient of restitution and a constant mean free path, it can be shown\* that

$$R = G\nu_0, \quad \dots\dots\dots(96)$$

where  $G = 2.6 \times 10^{-3}$ .

Equations (93) and (95) then lead to the result

$$M''/M = C_0\nu_0\delta\lambda_0/G, \quad \dots\dots\dots(97)$$

where  $\lambda_0$  denotes the equilibrium value of  $\lambda$  (the mean proportion of its energy lost by an electron at a collision) corresponding to the force  $Z_0$ .

We have also from (94) and (96):

$$\delta = \frac{1}{\sqrt{(1 + n^2/G^2\nu_0^2)}}. \quad \dots\dots\dots(98)$$

The above expression for  $M''$  is supported by the experimental results obtained by van der Pol and van der Mark at Eindhoven when investigating the modulation imposed on a signal from Bero-münster by the station at Luxemburg†. Their results are fitted by the curve whose equation is

$$\begin{aligned} M'' &= \frac{0.086}{\sqrt{\{1 + (n/780)^2\}}} \\ &= 0.086\delta, \end{aligned}$$

taking  $\nu_0 = 3 \times 10^5$  in formula (98) for  $\delta$ .

The theoretical relation obtained from equation (97) is

$$M'' = 0.119 \delta.$$

The agreement between the two coefficients 0.086 and 0.119 must be regarded as very satisfactory when the difficulty of evaluating a number of the quantities occurring in the calculations is taken into account; further, the value  $3 \times 10^5$  for  $\nu_0$  required to fit the experimental curve is in good agreement with the value suggested by a number of other experiments.

The modulation  $M''$  impressed on the second wave increases as the wave-length of the first wave is increased from about 500 to

\* Bailey and Martyn, *loc. cit.*

† See U.R.S.I. Report dated 10th Sept., 1934; and *Tijdschrift Ned. Radio Genootschap*, 7, pp. 12-17 (March, 1935).

2000 metres. At still higher wave-lengths it decreases, because very long waves are reflected in regions of the ionosphere much below those which reflect broadcast waves.

Further, the modulation  $M''$  is almost proportional to the power radiated by the first transmitter. For long-wave stations the radiated power must be of the order 100 kW to cause observable interaction. For example, the rated power of Luxemburg (1300m) is 150 kW, and the modulation impressed on Beromünster is only 0.086.

It is to be expected, however, from the calculations introduced in §6.4 that when the first wave is of approximately the same angular frequency as the local gyro-frequency the interaction will be considerably greater. We now proceed to calculate the power required for a gyro-wave to cause an appreciable effect on a second wave.

(ii) *The modulation impressed by a gyro-wave.*

As in §6.4 we need only consider the effect of the extraordinary component of the gyro-wave. The formulae derived above for  $M'$ ,  $M''$  and  $\delta$  hold, provided we substitute  $\bar{w}_e$  for  $\bar{w}_0$ , where  $\bar{w}_e$  is given by equation (88). Thus,

$$M'/M = 2\bar{w}_e\delta/\alpha R\nu_0,$$

and

$$M''/M = C_0\nu_0\delta\lambda_0/G.$$

For the purpose of calculation the following forms\* of these two equations are more convenient :

$$M'/M = \delta\bar{w}_e/(GT + \bar{w}_e), \quad \dots\dots\dots(99)$$

and

$$M''/M = C_0\nu_0\delta\bar{w}_e/(GT + \bar{w}_e), \quad \dots\dots\dots(100)$$

where  $T$  is the mean energy of agitation of an electron in the absence of electric fields ( $\doteq 5.8 \times 10^{-14}$  ergs).

The calculated values of  $\bar{w}_e$  given in table 34 show that this quantity becomes relatively negligible for values of  $y$  exceeding 5.5 km and values of  $N$  exceeding 200 electrons per cc. It is also clear from this table that  $\bar{w}_e$  is approximately constant, being roughly equal to  $2 \times 10^{-18}$  ergs (for  $Z = 5$  mV/m), at all points within a layer of the ionosphere about 4.5 km thick.

\* Bailey (1937).



In this region therefore,  $\nu$  is modulated at the frequency  $n/2\pi$ , and with a coefficient of modulation  $M'$  given by equation (99):

$$M' = 6.6 \times 10^{-3} \delta,$$

$M$  being taken equal to 0.5.

Near the top of this layer,  $\nu_0 = 7 \times 10^5$ ; so that at the audio frequency 256 cycles per second,  $\delta = 0.75$  and

$$M' = 0.5 \text{ per cent.}$$

The most favourable conditions are those under which appreciably all of the absorption of the second wave  $W''$  takes place in this region. Corresponding to the particular value of the angle of incidence  $i_o$ , the shortest wave-length  $\lambda''$  which  $W''$  can then have is that which causes the top of its trajectory to lie in the plane  $y = 4.5$  km, so that the highest value of the angular frequency  $\omega''$  is given by the formulae\*

$$\mu = \sin i_o, \quad \mu^2 = 1 - \frac{4\pi e^2 N}{m(\omega''^2 + \nu_0^2)}$$

where  $N = 90$  and  $\nu_0 = 7 \times 10^5$ .

We thus obtain the results set out in the first two rows in table 35. The corresponding attenuation coefficients given in the third row are calculated by means of the following formula given by Martyn†:

$$C_o \nu_o = 0.73 \cos i_o [0.57/(\omega'' \cos i_o)]^{1/5}.$$

The modulation  $M''$  impressed on  $W''$  is shown in the fourth row, and has been calculated by means of equation (100). In the last row are given the corresponding distances  $D$  from their source at which the waves  $W''$  are received, the formula used being

$$D = 200 \tan i_o \text{ km.}$$

We may now summarize our conclusions as follows:

For distances  $D$  greater than 350 km, signals having wavelengths exceeding 2300 metres can exhibit observable modulations caused by gyro-interaction‡ if their sky waves are reflected in regions of the ionosphere in the neighbourhood of the gyro-station.

\* D. F. Martyn, *Proc. Phys. Soc.*, **47**, p. 323 (1935).

† D. F. Martyn, *loc cit.*, p. 334.

‡ That is, radio interaction caused by a gyro-wave.

Similar observable modulations can occur with wave-lengths as short as 1300 m for distances exceeding 550 km, and as short as 600 m for distances exceeding 1100 km.

Table 35

$\omega''$  = maximum suitable angular frequency ;

$\lambda''$  = minimum suitable wave-length.

$i_o$	45°	60°	70°	80°
$\omega'' \times 10^{-5}$	2.9	8.1	14.1	30.2
$\lambda''$ (metres)	6500	2330	1340	625
$\exp(-C_o \nu_o)$	0.018†	0.085†	0.197	0.444
$M''$ (per cent.)	2.0	1.2	0.8	0.4
$D$ (kilometres)	200	346	550	1130

Thus, under favourable conditions, that is with freedom from atmospherics and on a suitable, unmodulated carrier-wave, the modulations impressed by a radio station with a power as low as 1 kW may be observed, provided that the frequency of this station is close to the value  $-He/2\pi m$ , where  $H$  is the total terrestrial magnetic field intensity at points of the  $E$ -layer roughly in the neighbourhood of the station,  $e$  being expressed in e.m.u.

It is of interest, also, to consider the problem of determining the least radiated power which under appropriate and practicable circumstances can influence the  $E$ -layer in an observable manner.

The first step in increasing the effectiveness of the vertical Hertzian aerial mentioned above is to place it horizontally, for this increases the maximum value of the electric intensity  $Z$  at the bottom of the  $E$ -layer by the factor 2\*. When the ground is a conductor it may partly neutralize this gain, but if the horizontal aerial is fixed at a height  $\lambda/4$  above the ground, where  $\lambda$  is the gyro wave-length, the effect of the ground conduction is,

† These results are only approximate, because Martyn's formula for the attenuation coefficient is not accurate for long waves.

\* This is due to a change, relative to the oscillator, of the radial distance of the affected part of the  $E$ -region by a factor  $\sqrt{2}$ , and a similar change of the zenithal angle from 45° to 90°.

if anything, advantageous. In this way the minimum power needed to cause observable interaction can be reduced to about 0.4 kW or less.

With a perfectly conducting ground, or with a suitable reflecting system of conductors placed on the ground below the horizontal aerial, the maximum value of  $Z$  is further increased by the factor 2, and so with relatively simple means the least power needed is about 100 watts.

This power can be reduced to 50 watts by adding a second horizontal Hertzian oscillator with its axis at right angles to that of the first, and maintaining equal currents in the two oscillators with phases differing by one-quarter of a cycle, so that a circularly polarized wave is radiated upwards from the aerial system.



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